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TRANSACTIONS

OF THE

ROYAL IRISH ACADEMY.

I. *Researches on the Nature and Constitution of the Compounds of Ammonia.*

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PART I.

ON THE SULPHATES AND NITRATES OF MERCURY, PARTICULARLY THE SUBSALTS FORMED BY AMMONIA.

HAVING shown in a former memoir that by the action of ammonia on the chlorides of mercury, there came into operation the principle which had been found by Dumas and Liebig to regulate the constitution of so many interesting bodies of organic origin,—that is to say, that by the elimination of one equivalent of hydrogen from the ammonia, and the union of the remaining hydrogen and nitrogen with the metal, there was generated an amide,—it became of importance to follow out into other combinations of the metallic salts with ammonia, an investigation which had led, in the few cases already studied, to such novel and interesting results. It is intended in the present memoir to investigate the functions of the ammoniacal elements of the mercurial subsalts, a department, of which, notwithstanding the labours of many chemists, our knowledge has remained imperfect, from circumstances similar to those which had led, in the same hands, to the conflicting opinions as to the nature of white precipitate already noticed.

In addition to the ammoniacal subsalts of mercury, there are described in the present paper the sub-sulphate and the sub-nitrates of the black and red oxides. And as the necessity of a new examination of these compounds may not appear to those who have not themselves studied the chemistry of the salts in detail, I may state, that in order to ascertain the part which the ammonia plays in the subsalts formed by its means, it became necessary to establish a comparison with the ordinary subsalts most analogous in composition; and on searching through the analyses of the mercurial subsalts already recorded, I found the testimonies so conflicting, and the results so imperfect, that I was obliged to commence the subject as if it had been actually new.

In the former memoir I assumed as the atomic weight of mercury the number 202.8, which supposes the corrosive sublimate to be a bi-chloride. This opinion I have since found reason to alter, from evidences, partly derived from the results contained in the present paper, and partly from other sources; I have therefore now adopted the Berzelian number 101.4, by which the calomel is looked upon as a sub-chloride, and sublimate as containing an equivalent of each ingredient. It will be found that by this arrangement the formulæ of these classes of compounds become much more simple than on the plan of the larger number, to which however they can easily be reduced.

Without occupying attention by any unnecessary prefatory matter, I shall pass at once to the analytical results.

I. OF THE SULPHATES OF THE RED OXIDE OF MERCURY.

Before commencing the study of the action of ammonia on the sulphates of mercury, I considered it proper to satisfy myself, by actual analyses, of the composition of these bodies, particularly with reference to the possible existence of water as one of their constituents, and the more so, as from the conflicting statements of chemists with regard to the nature of turpeth mineral, it was not unlikely that a source of error not previously unveiled might exist. As, however, my results have confirmed the ordinary view of the composition of these bodies, I will not detail any of the methods I employed, but merely state the absolute numerical results.

An analysis of neutral sulphate of mercury gave

	Experiment.	Theory $HgO.SO_3$
Sulphuric acid	= 26.72	26.82
Oxide of mercury	= 72.98	73.18
	99.70	100.00

Three analyses of turpeth mineral gave

	I.	II.	III.
Sulphuric acid	= 10.89	10.87	11.08
Oxide of mercury	= 88.71	89.24	88.76
	99.60	100.11	99.84

The theory of $HgO.SO_3 + 2\,HgO$ should give

Sulphuric acid = 10.91
Oxide of mercury = 89.09

I would not have brought forward even this notice of the numbers I obtained, were it not that from the high authority by which some of the incorrect results had been supported, and their insertion in some of the most approved elementary books, it might have appeared objectionable to make any one of the various formulæ given the foundation of a chain of reasoning, without having first established by experiment its superiority over the rest.

II. OF AMMONIA SUB-PERSULPHATE OF MERCURY.

When persulphate of mercury is treated by water of ammonia, it is converted into a white powder, which appears to be almost insoluble in water. In general, on the first addition of the water of ammonia, there is some turpeth mineral formed, which however gradually disappears, and the product is an uniformly white powder. This reaction takes place more rapidly by boiling, but the nature of the result is the same. If turpeth mineral be boiled, or treated in the cold with water of ammonia, it is converted into the same white substance, as shall be proved by the analyses subjoined. The existence of this white ammoniacal subsulphate was noticed by Fourcroy, but he made no analysis of it, nor has it ever been, at least to my knowledge, subjected to an accurate investigation.

This substance is heavy; it is not decomposed by water, which, however, dissolves some traces of it. When heated it becomes brown, exhales traces of ammonia, much water and nitrogen, and there finally remains sulphate of the black oxide of mercury, which by a further heat gives its usual products of decomposition. This powder is soluble in nitric and muriatic acids. When diffused through water, and treated by sulphuretted hydrogen, the mercury is all thrown down as sulphuret, while the liquor remains perfectly neutral, and gives by evaporation sulphate of ammonia.

I shall speak of this substance always as ammonia-turpeth, a name short, and not involving any theory, and therefore the best calculated for use.

To analyze this compound, the following methods were pursued:

A. 5.072 grammes ammonia-turpeth were dissolved in muriatic acid, and precipitated by muriate of barytes. The sulphate of barytes formed was washed until the water passed quite pure; it was then carefully dried and ignited, and weighed, when corrected for the ashes of the filter, = 1.223 gramme, or 24.11 per cent., containing 8.28 of sulphuric acid.

The liquors filtered off the sulphate of barytes were treated by sulphuret of hydrogen, and the sulphuret of mercury was collected on a filter, and carefully dried until it ceased to lose weight; when dried there was

$$\left.\begin{array}{lll}\text{Sulphuret and filter} & = & 5.835\\ \text{Filter} & = & 0.910\end{array}\right\}\ 4.925\ \mathrm{H}g\mathrm{s}.$$

giving $\mathrm{H}g.\mathrm{s} = 96.9$ per cent., or 83.69 mercury.

B. 10.375 grammes of sulphate of mercury were boiled with a considerable excess of ammonia, until completely converted into ammonia-turpeth, which was collected on a filter after the whole had been allowed to cool.

The powder was washed until the liquor ceased to give appreciable traces of sulphuric acid; it was then dried by a temperature of 212°, and weighed

$$\left.\begin{array}{lll}\text{Powder and filter} & = & 8.590\\ \text{Filter} & = & 0.361\end{array}\right\}\ 8.229\ \text{ammonia-turpeth.}$$

To the filtered liquor and washing was added an excess of muriate of barytes, it having been first acidulated by muriatic acid. The sulphate of barytes was collected on a filter and washed, as long as the liquors passed through containing muriatic acid; it was then dried and ignited. The ashes of the filter having been allowed for, it weighed 6.112 grammes.

The liquors remaining contained a trace of mercury, which precipitated gave 0.220 of $Hg.S$. Therefore 100 of sulphate of mercury gave

Ammonia-turpeth = 79.31
Sulphate of barytes = 58.91
$\because$ Sulphuric acid = 20.245
And sulphuret of mercury = 2.10 equivalent to 1.81 of mercury, giving 1.96 oxide and 2.68 sulphate.

There had therefore been decomposed 100—2.68 of the sulphate, and 100 of sulphate completely converted into ammonia-turpeth should give

Ammonia-turpeth = 81.48
Sulphuric acid = 20.06

The sulphuric acid in 100 of $HgO.SO_3$ is 26.82, of which 20.06 is almost exactly three-fourths, for $\frac{3}{4} . 26.82 = 20.115$. Therefore in the ammonia-turpeth is contained all the mercury and one-fourth of the sulphuric acid; its composition therefore comes out,

$$\left.\begin{array}{lcr} \text{Mercury} & = & 67.83 \\ \text{Sulphuric acid} & = & 6.76 \\ \text{Other matters} & = & 6.89 \end{array}\right\} 81.48, \text{ or } \left.\begin{array}{r} 83.25 \\ 8.29 \\ 8.46 \end{array}\right\} 100.00$$

C. 7.317 grammes of ammonia-turpeth were diffused through water, and decomposed by a current of sulphuretted hydrogen. The sulphuret of mercury was collected on a filter, and dried carefully, until it ceased to lose weight.

$$\left.\begin{array}{lcr} \text{Filter and sulphuret} & = & 7.422 \\ \text{Filter} & = & 0.355 \end{array}\right\} 7.067, \text{ or}$$

Sulphuret = 96.58 per cent., containing 83.35 mercury.

The clear liquor reacted neutral; it was evaporated in a water-bath to perfect dryness, and the capsule, with the residual sulphate of ammonia, carefully weighed; the salt then cleared out without loss, and the capsule tared; the salt was then again weighed on the tared slip of paper, on which it had been collected, and the second not differing from the first weighing by a milligramme, certainty of accuracy was obtained.

The sulphate of ammonia weighed 0.988 gramme, corresponding to 13.5 per cent., and consisting of

Sulphuric acid	=	8.18	13.50
Ammonia	=	3.48	
Water	=	1.84	

Tabulating the results of these three methods, there is obtained for ammonia-turpeth

		A.	B.	C.	Mean.
Sulphuric acid	=	8.28	8.29	8.18	8.25
Mercury	=	83.69	83.25	83.35	83.43
Ammonia	=			3.48	3.48
Oxygen and loss	=				4.84

The positive values obtained by analysis give the proportions in ammonia-turpeth to be:

1 atom of sulphuric acid.
1 atom of ammonia.
4 atoms of mercury.

But for the oxidation of the mercury there would be required (as, from the solubility of ammonia-turpeth in muriatic acid, the whole of the mercury is proved to be in percombination) oxygen = 6.582, a quantity which is altogether excluded by the sum of the values of the other ingredients, which leave room for only 4.84 of oxygen. Now this number is almost exactly three-fourths of 6.582, since $\frac{3}{4} . 6.582 = 4.937$; and we have consequently the most complete evidence that the fourth atom of metal is combined with some other negative radical than oxygen. If one conceives that in this ammonia-turpeth the azote and hydrogen exist as amidogene, the formula falls in accurately with the experimental results, for there is

SO_3	=	40.16	8.27	Analysis	=	8.25
NH_2	=	16.14	3.32		=	3.27
$4 Hg$	=	405.60	83.47		=	83.43
$3 O$	=	24.00	4.94		=	5.05
		485.90	100.00			100.00

By this formula 100 of sulphate of mercury should give 81.30 of ammonia-turpeth, while in experiment B there was obtained 81.48.

It will be seen that the formula $HgO . SO_3 + 2 HgO + Hg NH_2$ is completely analogous to that for the yellow powder formed by the action of water on white precipitate, if we write the sulphate of mercury as $Hg.SO_4$; then there is

$$Hg.Cl + 2\,HgO + Hg\,NH_2, \text{ and}$$
$$Hg.SO_4 + 2\,HgO + Hg\,NH_2.$$

We shall have occasion, hereafter, to advert to this type of a remarkable class of combinations.

III. ACTION OF AMMONIA ON SULPHATE OF BLACK OXIDE OF MERCURY.

When the sulphate of the black oxide of mercury is treated by cold or boiling water no reaction occurs indicating the formation of a basic salt; it would therefore appear as if there existed but one sulphate of the black oxide.

When sulphate of the black oxide of mercury is treated by water of ammonia there is obtained a dark grey powder, which, when heated, gives water, ammonia, sulphurous acid, oxygen, and mercury. It is thus indicated to be a basic salt, containing ammonia; but great difficulty was found in tracing accurately the proportions in which complete decomposition occurred.

To determine the nature of this grey compound, the following method was adopted:—A weighed portion of sulphate of black oxide of mercury, was treated by an excess of water of ammonia, until the reaction appeared to be complete, and a uniform dark grey powder was produced. It was then collected on a filter, and the liquors, which contained but a mere trace of mercury, were mixed and acidulated by muriatic acid, and precipitated by muriate of barytes. The sulphate of barytes was then collected and dried, and having been ignited, with its filter, weighed, and the correction for ashes made.

The results of five experiments of this kind are given in the subjoined table, the details being omitted, in consequence of my not intending to use these results as bases for induction, and therefore it not being necessary to specify the particulars of each case:

100 of $\underline{Hg}.O + SO_3$	A.	B.	C.	D.	E.
Grey Powder . .	Not determined.	83.08	92.5	90.22	88.89
Free SO_3	13.85	11.75	Not determined.	8.35	9.96

The sulphate of the black oxide of mercury is, when prepared by double decomposition, anhydrous, and is composed of

$$\left.\begin{array}{lcr} \text{Mercury} & = & 80.80 \\ \text{Oxygen} & = & 3.18 \\ \text{Sulphuric acid} & = & 16.02 \end{array}\right\} 100.0$$

But, from the extensive limits, within which the quantity of the sulphuric acid removed by the ammonia, is contained, it would be improper to assert positively by what formula the result should be expressed. I consider that by the action of the ammonia a certain quantity of a per-compound may have been formed, and thus have given rise to the variable nature of the result. The results A and B, however, tend to induce me to look upon the grey compound, when pure, as having the composition $\underline{Hg}O.SO_3 + 2\underline{Hg}O + \underline{Hg}NH_2$, and bearing the same relation to the ammonia-turpeth, that the powder formed by water of ammonia on calomel, bears to white precipitate. If one might hazard a conjecture, the other results would indicate a tendency to a limit in the decomposition, when the half of the sulphuric acid had been removed, and thus there may be a body also grey coloured $\underline{Hg}O.SO_3 + \underline{Hg}NH_2$, or rather $\underline{Hg}SO_4 + \underline{Hg}NH_2$, similar to $\underline{Hg}Cl + \underline{Hg}NH_2$, as described in the former paper.

I did not follow up any analysis of the grey powder, because it was evident, from the variable nature of the circumstances affecting its formation, that no result could be obtained, so closely true, as to prove either for or against the question of the function of the ammonia, or indeed the quantity of the latter constituent (never more than three per cent.), that might have been therein contained. It is necessary therefore, on this point, to allow of the temporary guidance of the analogical evidence, which we derive from the more fixed results of the analyses of corresponding compounds.

IV. OF THE NITRATES OF THE RED OXIDE OF MERCURY.

We owe to the younger Mitscherlich an examination of the nitrates of mercury, which constitutes, up to the present day, all our knowledge regarding them. The singularity of the results to which he arrived, rendered their repetition of importance, and the more so, as the doubts which had been thrown upon the correctness of his analyses of the ammonia-nitrates, by Soubeiran, rendered it necessary to confirm his formulæ before they could be assumed as data in an investigation like the present.

There can be obtained but one crystallized nitrate of the peroxide of mercury: this salt is formed in small prisms, which deliquesce, except in a very dry room; when dried between folds of blotting paper, the crystals taste metallic, but not acid. These crystals are decomposed by water, but only a portion of the mercury is thrown down as a pale yellow powder, whilst the liquor becomes acid. If the supernatant liquor be evaporated, the excess of acid is driven off, and there crystallizes, on cooling, the same salt as had been previously dissolved.

To analyze this salt, the same method was pursued as had been employed by Mitscherlich, and with exactly the same result. As the analyses were but confirmatory of his accuracy, I shall not enter into their details. The formula of this crystallized pernitrate of mercury is $\mathrm{Hg}O.NO_5 + \mathrm{Hg}O + 2HO$, and in numbers:

2 atoms of oxide of mercury	=	202.80
1 of nitric acid	=	54.14
2 of water	=	18.00
		274.94

It is well known that this salt is decomposed by water, but there still remains some doubt as to the constitution of the subnitrate thus generated. From the variable appearance it presents, according to the method by which it has been obtained, it evidently is not of constant nature; and it is generally stated by systematic writers, that by washing it can be completely resolved into nitric acid and oxide of mercury. Of this nitrous turpeth, as it has been generally termed, two quantitative analyses have been recorded, of which the results follow:

		Oxide of Mercury.	Nitric Acid.	Reference.	
Braancamp	=	88.0	12	An. Chim.	54
Grouvelle	=	88.97	11.03	An. Ch. et Phys.	19

These results coinciding so closely, and leading immediately to the formula $NO_5 + 4\,\mathrm{Hg}O$, might appear to be conclusive, but several circumstances induced me to consider a new examination necessary. Thus, all other analyses made by Braancamp were inaccurate by four or five per cent., a result to be partly attributed to the imperfect state of analytical chemistry at the time he wrote; and also, it appeared from the evidently inconstant nature of the subnitrates obtained by water, that the stages of its production required to be closely studied. In addition I had observed that nitrous turpeth, when heated, always yielded some liquid nitric acid; this fact should introduce water as one of its constituents, which the results obtained by Braancamp and Grouvelle necessarily exclude.

A quantity of crystallized nitrate of mercury was treated by water, and the undissolved portion washed by warm water until the washings no longer reacted acid. It then appeared as a fine yellow powder, very heavy, not acted on by cold water, but converted into a brownish red powder by boiling water, which dissolved out the soluble nitrate of mercury, not affecting blue cabbage paper. When this powder is heated, it gives much red fumes and a quantity of liquid nitric acid, and there remains red oxide of mercury, which by a stronger heat is decomposed. As, by avoiding the use of boiling water, this powder was obtained apparently similar in appearance and properties at different times, it was selected for analysis.

A. 5.458 grammes of this powder were dissolved in muriatic acid, and treated by proto-chloride of tin. There were obtained 4.170 grammes of metallic mercury, giving 76.40 Hg per cent.

B. 5.513 grammes of a portion prepared at a different time were dissolved in muriatic acid diluted with a good deal of water, and precipitated by sulphuretted hydrogen; there were obtained

$$\left.\begin{array}{lcl}\text{Filter and sulphuret} & = & 5.935\\ \text{Filter} & = & 0.932\end{array}\right\} = 5.003\ Hg\,S,$$

giving mercury = 78.31 per cent.

C. A portion of the yellow powder having been treated by boiling water, and having assumed a brownish red colour, was dissolved in muriatic acid, and precipitated by sulphuretted hydrogen. Thus analyzed, 4.975 of this powder gave 4.919 sulphuret of mercury, corresponding to 85.33 mercury per cent.

D. A quantity was boiled for a long time, until it had been converted into a brick red powder, which was analyzed by solution in muriatic acid and the separation of the mercury by proto-chloride of tin; from 7.746 grammes were obtained 6.673 mercury, or 86.17 per cent.

No matter how far the boiling might be carried, I could not reduce the powder to the state of pure red oxide. The residual powder dried always gave by heat red fumes, and also liquid nitric acid, but in constantly decreasing proportion. I consequently considered it unnecessary to press the series of analyses further.

The analyses A and B give the result $\mathrm{NO_5 . HO + 3HgO}$ pretty closely, the theoretical numbers being

$$
\begin{array}{lrr}
\left.\begin{array}{lcr}\mathrm{NO_5} & = & 54.14 \\ \mathrm{HO} & = & 9.00\end{array}\right\} & 63.14 & 16.13 \\
\left.\begin{array}{lcr}3\mathrm{Hg} & = & 304.20 \\ 3\mathrm{O} & = & 24.00\end{array}\right\} & 328.20 & 83.87 \\
\hline
 & 391.34 & 100.00
\end{array}
\left\{\begin{array}{lcr}\mathrm{Hg} & = & 77.74 \\ \mathrm{O} & = & 6.13 \\ \mathrm{NO_5} & = & 13.83 \\ \mathrm{HO} & = & 2.30 \\ \hline & & 100.00\end{array}\right.
$$

and I am disposed to consider such as being the real composition of the yellow sub-pernitrate prepared by water not boiling. It will be at once seen that this formula assimilates completely the sub-nitrate of mercury with those of copper and of bismuth, the nature of which has been lately elucidated by the experiments of Graham.

With regard to the red sub-nitrate prepared by boiling water, I am inclined to look upon it, in like manner, as having a definite composition, because, whilst the specimen used in analysis C had been boiled but for a few minutes, and that used in analysis D for some hours, their composition appeared to be quite the same. When heated, this red subsalt certainly yields a trace of water, besides nitrous acid fumes; but this water is in such small quantity that it might be considered as hygrometric. The quantity of mercury obtained, may serve equally well for one or other of two formulæ, thus:

$$
\begin{array}{lccc}
 & & \mathrm{NO_5 + 6HgO} & \mathrm{NO_5 . HO + 7HgO} \\
\text{Nitric acid} & = & 7.62 & 6.52 \\
\text{Oxide of mercury} & = & 92.38 & 92.39 \\
\text{Water} & = & & 1.09
\end{array}
\left.\begin{array}{c} \\ \\ \\ \end{array}\right\} = 100.0
$$

Although I have always found this red powder to give a trace of water, yet I incline strongly to the first of the above formulæ, to which I shall refer when treating of some analogous ammonia compounds.

As the composition assigned by Grouvelle to the sub-pernitrate falls within the limits of the two bodies which have been just described, it may be supposed that he had examined a mixture of them, and not a pure substance; this idea I consider probably to be true.

By the action of water on the crystallized pernitrate it is resolved into yellow sub-pernitrate and an acid-reacting salt, which, when evaporated, yields, as was already mentioned, the same crystallizable nitrate, whilst the excess of acid passes off. There takes place, therefore, a division of the mercury into two portions, one of which passes into solution, whilst the other is left in the insoluble yellow powder. The salt in solution does not appear to crystallize, but to give, on concentration, nitric acid and the crystallized basic salt of Mitscherlich. The proportion of mercury which remains in the solution approximated, in my trials, to one-third of that precipitated, and the action of water may be explained by the following formula:

$$2(\mathrm{NO_5}+2\,\mathrm{HgO}+2\,\mathrm{HO}) = \{\mathrm{HO.NO_5}+3\,\mathrm{HgO}\} + \{\mathrm{HgO.NO_5}+3\,\mathrm{HO}\}$$

The crystalline pernitrate being considered as a double salt, which is decomposed by water into its constituents. It may evidently be likewise considered as a simple salt, the sum of the number of atoms of hydrogen and mercury remaining still four, but capable of indefinite replacement within that limit.

The proportions of mercury and nitric acid in solution, after the precipitation of the yellow basic salt by water, must be quite definite, and should, if isolated, produce a salt $\mathrm{HgO\,.\,NO_5\,.\,HO}+2\,\mathrm{HO}$, corresponding to the ordinary nitrates of copper and bismuth, but which may be so easily decomposed as to be uncrystallizable. Moreover, if we look to the very general tendency to the formation of bodies containing four equivalents of mercury, it will appear not impossible but that a type of basic nitrates $\mathrm{HgO.NO_5\,.\,HgO}+2\,\mathrm{HgO}$ may really exist, and on which Grouvelle may have happened to alight, although I could not, even after many trials, succeed in preparing it.

Thus there should be a series of salts:

$\mathrm{HgO\,.\,NO_5\,.\,HO}+2\,\mathrm{HO}$. uncrystallizable.
$\mathrm{HgO\,.\,NO_5\,.\,HgO}+2\,\mathrm{HO}$. ordinary salt.
$\mathrm{HgO\,.\,NO_5\,.\,HO}+2\,\mathrm{HgO}$. yellow basic salt.
$\mathrm{HgO\,.\,NO_5\,.\,HgO}+2\,\mathrm{HgO}$. Grouvelle's basic salt.

and also

$\mathrm{HgO\,.\,NO_5\,.\,HgO}+4\,\mathrm{HgO}$. red basic salt.

V. OF THE AMMONIA SUB-PERNITRATES OF MERCURY.

It has been long known, that, by adding water of ammonia to a solution of pernitrate of mercury, there is obtained a fine white powder, which has been examined by Mitscherlich and Soubeiran, with results, however, so discrepant, as not to allow us to draw any conclusion whatsoever from them.

Almost immediately on commencing the examination of this reaction, I found that the nature of the precipitate obtained was liable to considerable variation, and that very trivial alterations in the conditions, under which the ammonia was added, changed the proportion of quicksilver by four or five in the hundred,—limits including the values obtained by the above-mentioned chemists. It therefore became probable that, as in the case of white precipitate, the existence of two or more different bodies had led to the discrepancies in the statements of those chemists; and by paying minute attention to the circumstances which influence their formation, I was led to detect the existence of three distinct ammoniacal subnitrates, as prepared by mere precipitation. The circumstances which influence the nature of the precipitate are, the concentration of the mercurial solution, its degree of acidity, the strength of the water of ammonia, the excess of one or other reagent, and the temperature. By slight changes of these, there are produced modifications of composition, and frequently an imperfect change from one to the other form takes place. In addition to these three precipitated compounds, there are two others obtained by crystallization, of which one had been examined by the younger Mitscherlich, and the other was met with first in the course of these investigations.

Ammonia Sub-pernitrate, No. 1.—When a dilute, and not very acid solution of pernitrate of mercury is treated by weak water of ammonia, (taking care not to add an excess of the latter, and the solution being cold,) there is obtained a pure milk-white precipitate, not granular, which remains suspended for a considerable time. This precipitate, collected on a filter, may be exposed to a heat of boiling water without change, and is consequently easily dried.

When this powder is heated, it becomes yellow, and gives azote, ammonia, then red fumes, and finally oxygen and quicksilver. If boiled with water, it becomes granular and heavier, deposits itself more easily, and has lost, in some degree, its pure white colour. The water remains neutral, but is found to hold some nitrate of ammonia in solution.

On analysis, this powder yielded precisely the same results as had been obtained by the younger Mitscherlich; on that account I shall not insert the details of the methods, which in great part resembled those already described in the analyses of ammonia-turpeth, but shall merely note the quantities of mercury and other constituents obtained.

In three analyses there resulted:

		I.	II.	III.
Mercury	=	76.50	76.84	75.9
Nitric acid	=	12.66		
Ammonia	=	4.01		

These three portions had been prepared and analyzed at different periods.

The formula $NO_5 + NH_3 + 3HgO$ gives

3 atoms	mercury	=	304.20	76.17
3 „	oxygen	=	24.00	6.01
1 „	nitric acid	=	54.14	13.54
1 „	ammonia	=	17.14	4.28
			399.48	100.00

Mitscherlich's result was

Mercury = 75.55
Nitric acid = 14.33
Ammonia = 4.68

There can, therefore, be no doubt of this being really the composition of the substance, and if we compare it with the yellow sub-pernitrate, we shall observe a very curious analogy. Thus the water in the common subnitrate is replaced by ammonia, that is, by amide of hydrogen, so that the basic function which has been so elegantly shown by Mitscherlich and Graham to belong to water, appears to be enjoyed in a certain degree by ammonia also. This is shown, and the nature of this white substance very elegantly proved, by an experiment well calculated for class illustration: if some of the water subnitrate be put into a solution of nitrate of ammonia, and boiled for a moment, the white powder is rapidly formed, and the liquor will be found to be strongly acid. Thus,

$$(HO \,.\, NO_5 + 3HgO) + NO_5\,NH_3 = (NH_3 \,.\, NO_5 + 3HgO) + HONO_5.$$

Of the Ammonia Subnitrate, No. 2.—It having been found that, by boiling the former powder with water, it altered in its appearance, and became much heavier and more granular, it was natural to expect from it a different constitution. If the solutions of nitrate of mercury and of ammonia be mixed, while hot, or if they be boiled after mixture, the same modification is produced; and as Soubeiran had been led astray by the effects of boiling white precipitate, it might be inferred that his discordant results arose from his operating with hot solutions in this case also. The powder, thus prepared, gives the same results of decomposition as the former; potash, even boiling, exerts no action on either, giving out no ammonia, and no oxide of mercury separating. The following analyses were made:

A. 7.185 grammes were dissolved in muriatic acid, and the solution precipitated by sulphuretted hydrogen. The sulphuret produced weighed 6.766, or 94.17 per cent., containing 81.24 of mercury.

B. 7.353 of another portion were dissolved in muriatic acid, and the mercury precipitated by proto-chloride of tin. There were obtained 5.978 grammes, being 81.28 per cent.

When this powder, diffused through water, is treated by sulphuretted hydrogen, there is formed sulphuret of mercury, and the liquor contains neutral nitrate of ammonia.

From these results, and the quantity of quicksilver coinciding so closely with that obtained by Soubeiran, there is no doubt but that the substance is the same as that upon which he operated.

The formula given by Soubeiran is $NO_5 + NH_3 + 4HgO$, which gives the numbers

$4Hg$	=	405.60	79.71
$4O$	=	32.00	6.29
NO_5	=	54.14	10.63
NH_3	=	17.14	3.37
		508.88	100.00

He however obtained 80.08 mercury per cent., or more than he should by his formula; and he proved that the nitric acid and ammonia could not exist in the powder as common nitrate of ammonia. Indeed he expressly states that the clearing up the nature of the function played by ammonia in these combinations should be left to a future period in science. Under these circumstances there can be no doubt but that the true formula for Soubeiran's subnitrate is as follows: $HgO.NO_5 + 2HgO + HgAd$, which gives

$4Hg$	=	405.60	81.13
$3O$	=	24.00	4.81
NO_5	=	54.14	10.83
NH_2	=	16.14	3.23
		499.88	100.00

This compound resembles those already described containing chlorine and sulphuric acid.

By using strong nitrate of mercury, and a considerable excess of a strong solution of ammonia, I have on two occasions obtained a yellowish white precipitate, yielding between 84 and 85 per cent. of mercury, and containing nitric acid and ammonia in the proportions of one equivalent of each. I have not, however, discovered the circumstances under which this third modification may be generated at will, for in trying often to form it, sometimes by hot liquors, at other times using the solutions cold, I have obtained the substances previously described, or else mixtures of them. The existence, however, of a yellowish white powder containing more mercury than either, is certain, and I consider its formula to be probably

$$(HgO.NO_5 + 4HgO + HgAd),$$

I shall not, however, dwell upon it more; the relation which it holds to the red sub-pernitrate is quite evident.

The Crystalline Ammonia Subnitrate.—Mitscherlich had observed that if the ammonia subnitrate of mercury be boiled with an excess of ammonia, and nitrate of ammonia be added, a portion of the powder dissolves, and the liquor, when it cools, yields, according as the excess of ammonia passes off, small crystalline plates of a pale yellow colour. I have verified this observation, but I did not analyze those plates, because I could form but a very small quantity of them; and having found in all cases that Mitscherlich's analyses were remarkably good, I considered that in the case of these crystals, which I found great difficulty in preparing, I might rely upon his accuracy. He found these crystals to be $NH_3.NO_5 + 2HgO$. But while I believe the numbers to be true, I do not consider that to be the rational formula. These crystals are formed by the solution of Soubeiran's subnitrate in nitrate of ammonia, and the formula is

$$(\mathrm{HgNO}_6 + 2\,\mathrm{HgO} + \mathrm{HgA}d) + (\mathrm{NH}_4\mathrm{O}\,.\,\mathrm{NO}_5),$$

which is equal to twice

$$(\mathrm{NH}_3\,.\,\mathrm{NO}_5 + 2\,\mathrm{HgO}).$$

That such is its constitution will be clearly shown from the study of the body next to be described.

When Soubeiran's ammonia subnitrate is boiled in a strong solution of nitrate of ammonia it is dissolved in considerable quantity, and the liquor being filtered while hot, deposits, on cooling, small but very brilliant needles, which after some time lose their lustre, and become dull and opaque, an appearance which the salt, when rapidly formed from a very strong solution, occasionally possesses from the commencement. This salt, after it has been once dried, cannot be again brought into contact with water without decomposition; its constituents are reproduced, the nitrate of ammonia dissolving, and Soubeiran's subnitrate being left undissolved. These circumstances rendered a few analyses sufficient for determining its composition.

A. 6.061 grammes of this salt were diffused through water, and decomposed by a current of sulphuretted hydrogen gas. The sulphuret of mercury was collected on a filter, and having been carefully dried, weighed 4.187, corresponding to 69.08 sulphuret and 59.60 mercury per cent. The liquor and washings, evaporated to dryness, in a water-bath, gave 2.173 of nitrate of ammonia, therefore 35.85 per cent.

B. 5.973 of a quantity prepared at a different time were dissolved in muriatic acid, and treated by sulphuretted hydrogen. The sulphuret was cautiously dried until it ceased to lose weight, and amounted to 4.010, giving 67.13 sulphuret, and 57.99 mercury per cent.

Hence there is

Mercury, mean value = 58.79
Nitric acid = 24.17
Ammonia = 7.65

If we divide these numbers by the atomic weights of the bodies, and reduce them to a standard, we shall find that there are almost exactly three atoms of nitric acid, three of ammonia, and four of mercury.

The formula $3(NH_4O \,.\, NO_5)+4Hg\mathit{o}$ gives

$4Hg$	=	405.60	59.78
$4O$	=	32.00	4.72
$3NH_3$	=	51.42	7.58
$3NO_5$	=	162.42	23.94
$3HO$	=	27.00	3.98
		678.44	100.00

I do not consider the rational formula of this compound so simple as should appear from the above expression. It is most likely to contain the ammoniacal subnitrate ready formed; it being decomposed by contact with water, and yielding that substance. If the mercury be as Soubeiran's subnitrate, the formula presents a curious relation; thus,

$$3(NH_4O \,.\, NO_5)+4HgO=$$
$$(NO_5 . HgO+2HgO+HgAd)+2(NO_5 . HO+2HO+HAd).$$

The facility with which this salt may be formed by heating red oxide of mercury with nitrate of ammonia might be used as an argument for the former view.

VI. OF THE NITRATES OF THE BLACK OXIDE OF MERCURY.

In the memoir to which I have had so frequently occasion to refer, George Mitscherlich described two crystallized proto-nitrates of mercury, and gave detailed analyses of them. I have had occasion to confirm his results, and I consequently consider the composition of these two salts as well established. I shall not describe any of my own analyses of them, but merely insert the formulæ derived from the numbers of Mitscherlich, in order that the substances, next to be examined, may be compared with them.

The salt obtained in transparent rhombs from an acid liquor has the formula $(\underline{Hg}O+NO_5)+2HO$, and consists of

Black oxide of mercury	=	74.54	100.00
Nitric acid	=	19.09	
Water	=	6.37	

When this salt is digested with more black oxide of mercury, or when an acid solution of it is left standing on an excess of mercury, the crystals which are deposited are opaque and white, they are generally rhombic prisms. The second (dimorphous) variety described by Mitscherlich I have not analyzed. Their formula is $3\underline{Hg}O + 2NO_5 + 3HO$, and their composition

$$\left.\begin{array}{lr} \text{Black oxide of mercury} & = 82.40 \\ \text{Nitric acid} & = 14.08 \\ \text{Water} & = 3.52 \end{array}\right\} 100.00$$

I shall hereafter point out some reasons for considering this to be a double salt.

It had been long since remarked that these crystallizable salts were decomposed by water, but great discordance had arisen among chemists as to the nature of the subsalts thus produced. On treating the crystallized nitrates by cold water there remains undissolved a white powder, which as long as the supernatant liquid is acid retains its colour, but if it be washed it becomes yellow. Further, if it be boiled, the brilliancy of the colour is injured, and by long-continued boiling it is converted into a grey powder, which, according to some writers, must be considered as a basic salt. These various phenomena it is necessary to study in detail.

The white powder, which is formed by the first action of water, I could never obtain in a form justifying any inference from an analysis of it. It is evident that, without freeing it from the liquor holding in solution a quantity of another salt, it would be useless to examine it; and on the other hand, by washing, the change from white to yellow cannot be avoided; it was thence necessary to consider the yellow subsalt, as being the product to which attention should be paid.

This yellow sub-protonitrate of mercury can be easily prepared: the white precipitate of which I spoke may be washed with cold water repeatedly, until it is converted into a bright lemon-yellow powder; by the use of warm water the change may be much accelerated, and the materials may be even boiled for some time without danger, provided that the liquors be not too often changed. The limit is known to have been passed when the brilliant yellow is dimmed by the supervention of a greyish shade. By a very cautious addition of a weak solution of potash, the quantity obtainable from the soluble salt may be very much increased, but the specimens thus prepared are seldom so completely bright and pure as where water alone has been employed in its preparation.

This salt, when heated, gives out red fumes and drops of liquid nitric acid, and leaves red oxide of mercury, which by a further application of the heat is decomposed. It is insoluble in water, and by boiling, is changed into a grey powder, which by the lens is seen to consist chiefly of quicksilver in the metallic state, and the liquor is found to contain some mercury, as nitrate of the red oxide.

Grouvelle has published the results of an analysis of this subnitrate. It is to be regretted that this chemist communicates no details as to his methods, since without them the degree of confidence which should be given to his results cannot be easily ascertained. He states this subnitrate, whether prepared by water or by potash, to consist of

$$\left.\begin{array}{lll}\text{Black oxide, 2 atoms} & = & 88.6\\ \text{Nitric acid, 1 atom} & = & 11.4\end{array}\right\} 100$$

These are the numbers given by theory, and it is very much to be condemned that a chemist should publish that he established a formula by analysis, without giving the details of a single experiment, or stating how close to the theoretic numbers he had actually arrived. In fact I considered that the composition of this body required to be determined, as if it had been perfectly untried.

The following analyses were made to determine its composition :

A. 6.305 grammes of a quantity prepared by hot water, without boiling, gave, treated by proto-chloride of tin, 5.217 mercury, or 82.74 per cent.

B. 4,927 grammes of a quantity prepared by cold water, gave, when treated by proto-chloride of tin, 4.086 mercury, or 82.93 per cent.

C. 6.513 grammes of a different portion was dissolved in muriatic acid, and the liquid much diluted; it was then decomposed by sulphuretted hydrogen, and the sulphuret collected, carefully dried, and weighed with the filter. There was obtained 6.312 sulphuret, or 96.91 per cent., containing 83.7 mercury.

It is abundantly evident that this salt contains some water as constitutional, for when heated, it always yields, in addition to the red fumes, a dew of liquid nitric acid. Assuming, therefore, the nitric acid to exist in the salt combined with an equivalent of water, we obtain the formula $NO_5 . HO + 2\underline{Hg}O$, which gives

$2\underline{\mathrm{Hg}}$	=	405.60	83.67
$2\mathrm{O}$	=	16.00	3.30
NO_5	=	54.14	11.17
HO	=	9.00	1.86
		484.74	100.00

and which is abundantly confirmed by the reactions of the body and by the quantity of mercury, which analysis indicated it to contain.

When a solution of proto-nitrate of mercury has been kept for a long time, there are frequently deposited in it a fine lemon-yellow crystalline salt, of great brilliancy. I have never seen the crystals larger than pins' heads, and they have been always too closely aggregated to allow of an accurate determination of their form. They react, in every respect, similarly to the powder just described, and their composition was determined by the following analysis:

6.257 grammes were dissolved in muriatic acid, and the solution having been considerably diluted, was treated by sulphuretted hydrogen. There was obtained 6.038 of sulphuret, being 96.5 per cent., containing 83.28 of mercury. Hence the formation of these crystals is evidently owing to the very gradual deposition of the basic salt from an acid liquor, and they are of the same nature as the powder rapidly prepared.

It will be seen that in this basic salt the law of replacement of water by metallic oxide holds, although the absolute number of atoms is quite different. It was found that the first crystallized nitrate of the black oxide had for its formula

$$\underline{\mathrm{Hg}}\mathrm{O}\,.\,\mathrm{NO}_5 + 2\mathrm{HO};$$

and the yellow basic salt is now proved to be

$$\mathrm{HO}\,.\,\mathrm{NO}_5 + 2\underline{\mathrm{Hg}}\mathrm{O}.$$

Moreover the second crystallized salt was shown to be, from Mitscherlich's analyses, as well as my own,

$$2\mathrm{NO}_5 + 3\underline{\mathrm{Hg}}\mathrm{O} + 3\mathrm{HO} =$$
$$\{\underline{\mathrm{Hg}}\mathrm{O}\,.\,\mathrm{NO}_5 + 2\mathrm{HO}\} + \{\mathrm{HO}\,.\,\mathrm{NO}_5 + 2\underline{\mathrm{Hg}}\mathrm{O}\}.$$

Hence, as was before alluded to, there is great reason to suppose the second crystallized proto-nitrate to be a double salt, consisting of the first and of the yellow basic salt, united in the proportion of an equivalent of each.

It would be an exceedingly interesting point to determine whether the three salts thus found to be generated by the replacement of successive equivalents of water by metallic oxide, and *vice versâ*, possess any simple crystallographic relation to one another. It would be highly important to determine, if the elements thus replacing one another influence the crystalline form of the salt, for if the metallic oxide which replaces water belong to the same isomorphous family, there should exist identity of form amongst those salts, provided the sum of the number of equivalents of water and metallic oxide remains the same.

If the yellow subnitrate be boiled with much water, in successive portions, it becomes grey, but that alteration is always accompanied by the separation of metallic mercury and the formation of pernitrate. Likewise, if potash be added to the yellow subnitrate it becomes grey, but there is produced a mixture of black oxide and unaltered salt. Thus no positive limit can be found indicating the existence of a blackish or grey sub-protonitrate of really definite composition, and I consider that Donovan and Grouvelle, who had asserted its existence, had been misled by the properties of a mixture of black oxide or of mercury with the subnitrate just described. Indeed Grouvelle, in his paper on the Basic and Acid Nitrates, does not mention this grey subnitrate at all; but Soubeiran, in discussing the composition of Hannehman's soluble mercury, asserts that it contains the blackish subnitrate described by Grouvelle, of which he gives a formula with numbers, which, by typographical errors, is rendered quite unintelligible, and I have never been able to meet a notice of it elsewhere. It shall be shown, moreover, in the next article, that the nature of Hannehman's mercury is quite different, and hence that ground for supposing a grey sub-protonitrate to exist can no longer hold.

I therefore conclude that there exists but one basic nitrate of the black oxide of mercury, that which may be obtained as a lemon-yellow powder, or in minute crystals of the same colour, and whose formula is $\mathrm{HO.NO_5} + 2\underline{\mathrm{Hg}}\mathrm{O}$.

VII. ON THE AMMONIACAL SUBNITRATE OF THE BLACK OXIDE OF MERCURY.

The study of the reaction of water of ammonia on the protonitrate of mercury presents great difficulties, in consequence of the facility with which the most important products of it are liable to change, and the consequent admixture of substances, which have their origin in the secondary decompositions of those at first formed; hence we find very irreconcileable statements put forward as to the nature of the black powder, which is the more immediate product of this action, by one chemist it being looked on as a mere oxide, by another as a subnitrate, whilst the analyses of George Mitscherlich, to whose accuracy I have had occasion so often to bear witness, showed that it did really contain ammonia and nitric acid among its elements. I am inclined to believe that Soubeiran himself now admits the incorrectness of his former statements, since in his Nouveau Traité de Pharmacie, he adopts the results of Mitscherlich, without at all adverting to the conclusions which he had advanced in his own paper on the subject.

When, to a solution of protonitrate of mercury, there is added water of ammonia, the precipitate, which at first is of a velvety black colour, gradually changes, passing through various shades of grey, until it becomes nearly white, and its state of aggregation varies in a similar manner: the portions first formed are heavy, and rapidly deposit, but according as the colour becomes lighter, it remains long suspended, at least the whitish portion, whilst a heavy grey powder falls more quickly down.

Having satisfied myself, by treating portions of these precipitates, of various shades of black and grey, with sulphuretted hydrogen, that the liquor contained, after separation of the quicksilver as sulphuret, nitrate of ammonia neutral, proving that an equal number of equivalents of nitric acid and ammonia were present in the precipitate; and having found, moreover, so great difficulty in decomposing the last portions as to render this method unavailable in obtaining a quantitative result, I resolved to examine minutely the influence which the variations in shade had on the quantity of mercury which the precipitate might contain; a result which very simple considerations will show, to lead to a complete knowledge of the nature of the body under examination.

A dilute solution of pure protonitrate of mercury was taken, and there was added to it a quantity of weak water of ammonia, about one-fourth of what would suffice for its complete decomposition. A considerable mass of a fine glossy black powder fell, which was collected on a filter, washed carefully, and dried at a temperature not exceeding 100° F. To the liquor separated from this first portion was added another quantity of water of ammonia, and thus another portion of precipitate obtained, differing but very little in shade, from the first; this having been likewise collected, the liquor was treated by a third quantity of water of ammonia, by which a precipitate was produced of a dark grey colour; after this had been removed, the remaining liquor was completely decomposed by an excess of water of ammonia, and thus a precipitate of a grey colour was obtained.

There had been thus collected, from the one solution of protonitrate, four portions of precipitate, which had gradually become lighter in colour according as the quantity of ammonia added had increased; numbering them in the order in which they had been prepared, they were subjected to analysis:

A. 7.748 of No. 1, dissolved in muriatic acid, gave, by proto-chloride of tin, 6.374 of mercury, or 82.27 per cent.

B. 9.456 of No. 1 gave, treated in a similar manner, 7.791 mercury, or 82.39 per cent.

C. 6.403 of No. 2, dissolved in muriatic acid, and decomposed by proto-chloride of tin, gave 5.410 mercury, or 84.49 per cent.

D. 7.093 of No. 3 gave, by proto-chloride of tin, 6.141 of mercury, or 86.7 per cent.

E. 7.943 of No. 4 gave, similarly treated, 7.067 mercury, or 88.97 per cent.

These results, tabulated, are:

Order of Formation.	Colour.	Mercury in 100.
1	Fine black.	82.27. 82.39
2	Greyish black.	84.49
3	Deep grey.	86.70
4	Grey.	88.97

The result of Mitscherlich's analysis are shown here, in order to understand how far his numbers are reconcileable with mine; he obtained

$$\left.\begin{array}{lcr} \text{Mercury} & = & 85.57 \\ \text{Ammonia} & = & 2.46 \\ \text{Oxygen} & = & 3.38 \\ \text{Nitric acid} & = & 7.32 \end{array}\right\} 98.73$$

Hence he deduced the formula $NO_5 . NH_3 + 3\underline{Hg}O$, which should give

$$\left.\begin{array}{lcr} \text{Mercury} & = & 86.46 \\ \text{Ammonia} & = & 2.43 \\ \text{Oxygen} & = & 3.43 \\ \text{Nitric acid} & = & 7.68 \end{array}\right\} 100.00$$

In any ordinary case, where the error, unavoidable in manipulation, and to which the collection of mercury in the metallic form by proto-chloride of tin, is peculiarly liable, should necessarily tend to diminish the quantities obtained, and consequently reduce the experimental, below the theoretical numbers, his analysis should be considered as completely establishing the formula; but here, there are other circumstances which require to be taken into account, and which will lead us to an opposite conclusion.

It is evident that in the preparation of Hannehman's soluble mercury, there is a tendency to error from the intermixture of a greyish material, and where the whole, or nearly the whole of the solution has been precipitated at once, this intermixture is unavoidable; hence it is only the first portions that can be obtained of the fine black colour which characterizes the pure substance. Now it has been fully proved, that according as the decomposition proceeds, the quantity of mercury in 100 increases in proportion as the colour becomes less deep; and hence the error, in estimating the composition of this body, must be opposite in direction to what generally occurs, and must tend to render the proportion of quicksilver above the truth. Thus, the result of Mitscherlich's theory is almost precisely that obtained in my analysis of specimen No. 3, which was not black, but dark grey; and Mitscherlich himself indicates the powder which he analyzed as grey; he says, "Nach dem Trocknen ist die Farbe des Pulvers grau und es darf sich kein metallisches quecksilber mechanisch herausdrucken lassen;" and also, if the solution which I employed had been precipitated all at once, there should have been a dark grey precipitate, and its composition should have been the mean of the composition of the powders given by the four equal and successive additions of water of ammonia, which average would almost coincide with the result which Mitscherlich obtained. So marked is the production of this whitish matter, that Soubeiran collected and analyzed it, and concluded from his results that it was an ammonia sub-protonitrate with the formula $NO_5 . NH_3 + 4\underline{Hg}O$. He now appears to have tacitly abandoned this opinion, and properly, for there is no doubt but that this white powder is a compound of red oxide, and is one or other of the bodies which have been already described in this paper. When treated with iodide of potassium it gives a reddish yellow powder, and it dissolves gently in muriatic acid, without the disengagement of any red fumes indicating a transition to a ~~higher~~ degree of oxydation. At the same time that this white per-compound is formed there is always some metallic mercury set free, which can generally be recognized in the grey specimens by using a lens, but the quantity is seldom so large as to allow of its mechanical separation by the application of pressure only.

From all these circumstances it is evident, that the specimens of Hannehman's soluble mercury, which are of the finest black in colour, are generated under the circumstances most favourable to their perfect purity. And as all the chances of error, except that of analysis, tend to increase the value of mercury, it results, that where the error of manipulation affects all equally, the lowest estimate should be that nearest to the truth. Hence I feel justified in assuming, with some confidence, that the numbers 82.27 and 82.39 are those by which the true formula may be established, and we must therefore consider Hannehman's soluble mercury to be the ammonia sub-nitrate,

$$NH_3 . NO_5 + 2\underline{Hg}O,$$

which should give 82.29 mercury per cent., and evidently corresponds to the yellow subnitrate formed by water, which has been proved to be

$$HO . NO_5 + 2\underline{Hg}O.$$

Note.—It has been very gratifying to me to find that Ullgren, who undertook, under the direction of Berzelius, to control the analyses contained in my first memoir on the Ammonia Compounds, has verified, even to the most minute point, all the results which I then brought forward. I did not receive the Jahresbericht for 1837, containing Berzelius's observations, until this first part of the present memoir had been partly printed, and hence could not earlier introduce any note of the suggestions which he makes. In Germany or Sweden it will not be necessary to adopt the word *amidogene*, as the word *amide* harmonizes better with chlor. cyan. iod. and others; but in English and French it is preferable that there should be a termination, as in cyanogene and oxygene, the final *ide* being in these languanges restricted to binary compounds. I shall, however, for the future adopt his terms of *amidides* and *amidurets*, as I consider them still more expressive of the nature of the bodies, and more directly formed from *amidogene* than the word *amides*.

PART II.

ON THE AMMONIACAL COMPOUNDS OF COPPER AND ZINC, AND ON THE BASIC CHLORIDES AND SULPHATES OF THOSE METALS.

IN developing the real nature of the series of quicksilver combinations which contain ammonia or its elements, it was found, that the quantity of the metal present, from its large equivalent number, preponderated so considerably over that of the other constituents of the various bodies analyzed, as to render the absolute exclusion of all theoretical views but that ultimately found correct, extremely difficult, and it was consequently my object, from the commencement, to re-examine in detail the ammonia compounds of certain metals with smaller atomic weights, in order, by an accumulation of numerical facts, to lay the foundation for a true theory of this class of combinations.

The group of metals, the compounds of which are discussed in the present section, is one exceedingly natural, and possessed of characters, particularly in relation to ammonia, which, when compared with those exhibited by quicksilver, should lead the chemist to expect the most remarkable results. Whilst the precipitates given by quicksilver solutions with ammonia are insoluble in an excess of the precipitant, those given by the metals now to be examined easily redissolve, and the peculiar character of the zinc compounds redissolving in an excess of the fixed alcalies, presents a point of contact, the study of which must be of the highest interest.

It will be found that I have connected with the analyses of the ammonia compounds, the examination of a number of basic salts, and of other substances which do not contain ammonia. Generally speaking, I was obliged to occupy myself with these bodies, in order to elucidate difficult passages in the history of the ammonia compounds, and though I have often apparently wandered from my way for the purpose of obtaining either a more elevated point of view, or a more extensive basis for analogical deductions, yet as the discovery of such bodies will be found, I trust, to present so many new facts in science, the proofs of their existence and composition will be given in this memoir, whilst I shall avoid as much as possible entering into any speculations concerning their real nature, as the views to which I have been led by these and previous investigations will require to be developed in a distinct section.

I. OF THE AMMONIACAL SULPHATE OF COPPER.

The composition of this body has been given by Berzelius, and I have found his result to be rigidly correct; I shall therefore not bring forward any details of my own analyses, but assume as true the formula

$$SO_3 . CuO + 2NH_3 + HO.$$

This salt crystallizes in right-rhombic prisms, which are complex macles, and I have not been able to determine the form really belonging to it. The crystal would appear to be produced by a number of rhomboidal plates, uniting at the edges, and leaving very often the centre hollow, but destitute of any other definite cleavage or direction.

When we consider the manner in which this salt is formed, we cannot look upon the oxide of copper as being united with the sulphuric acid. On adding water of ammonia to a solution of sulphate of copper, the action consists in the gradual separation of more and more sulphuric acid from the copper, and when, by an excess of alkali, the precipitate is redissolved, there is nothing in the reaction tending to make the oxide of copper go back again, but rather the reverse. Hence I will apply to this body the formula

$$(NH_3 . HO)\, SO_3 + (NH_3 . CuO);$$

that is, I consider it as being sulphate of ammonia, with which is united oxide of copper and as much more ammonia.

When this substance is exposed to the heat of an oil-bath, or of a carefully regulated spirit-lamp, it gives out ammonia and water, and if the heat be not carried beyond 300°, there remains a fine apple-green powder. When this powder is further heated the result varies according to the manner in which the heat is applied; if rapidly, there is given out ammonia and sulphate of ammonia, whilst sulphate, with oxide and suboxide of copper, remain behind; but if slowly, and that it be not carried beyond 500° F., the remainder of the ammonia can be gotten rid of, and sulphate of copper quite pure will remain behind, there being no water disengaged in this latter period of the process.

To determine the exact nature of this decomposition, the following experiments were made:

A. 1.969 grammes of crystals were reduced to fine powder, and heated, until water ceased to be given off. It was in the state of a fine green powder, which weighed 1.545, or 78.47 per cent.

B. 4.921 of finely powdered crystals were heated in a precisely similar manner; there remained 3.854, or 78.32 per cent.

C. 5.042 grammes treated similarly, gave 3.921, or 77.77 per cent.

D. 2.991 grammes were heated very cautiously, until all ammonia and water were expelled; a mere trace of sulphate of ammonia had formed, and there remained 1.947 of sulphate of copper, or 65.1 per cent., which redissolved almost totally in water.

The theoretical composition of the ammonia sulphate is:

SO_3	=	40.16	32.58
CuO	=	39.60	32.22
$2NH_3$	=	34.28	27.89
HO	=	9.00	7.31
		123.04	100.00

which by heat evidently breaks up into

$CuO.SO_3$	=	64.80	and	HO	=	7.31
NH_3	=	13.95		NH_3	=	13.94
		78.75				21.25

Thus it is demonstrated by experiment, that by the first action of heat all the water of the ammonia sulphate is expelled with half of the ammonia, and there remains the green powder, consisting of sulphate of copper and one equivalent of ammonia, which last, by a further application of the heat, may be driven off. I endeavoured by a cautious application of heat to separate the water without losing the ammonia, but found it impossible to effect it. In this case, therefore, the copper does not exist as amidide, but on referring to the formula

$$(NH_3 . HO)\ SO_3 + (NH_3 . CuO)$$

it is evident that the sulphuric acid is inserted between two equivalent groups, which are related to one another, through the replacement of hydrogen by copper; the acid had been in the crystals more immediately united with that which represents oxide of ammonium, but on the application of heat, the previous affinities were subverted, and, the acid remaining in union with the group of more permanent constitution, the elements of the ammonia and water are set free, the formula of the green powder being

$$(NH_3 . CuO) . SO_3 .$$

Graham had already pointed out, that when ammoniacal gas is passed over sulphate of copper at a high temperature, but half an equivalent is absorbed, and hence he hazarded the idea, that the resulting compound might be analogous to an ordinary double sulphate, as

$$CuO . SO_3 + (NH_3 . CuO)\, SO_3$$

corresponding to

$$CuO . SO_3 + (NH_3 . HO) . SO_3 .$$

This body can likewise be obtained when the action of the heat on the ammoniacal sulphate of copper is kept below 400° F.; there are given off three-fourths of the ammonia with the water, and there remains $2(SO_3 . CuO) + NH_3$.

It is well known that the sulphate of copper in the cold absorbs two and a half equivalents of ammonia, and the resulting body warmed loses two, corroborating fully the view originally struck out by Graham, and to which my results lend considerable support.

If the apple-green powder be exposed to the action of damp air it gradually becomes blue, from the absorption of water, but the process is very slow; if, on the other hand, the powder be moistened with a small quantity of water, much heat is evolved, and a full blue colour produced; if there be any water in excess it may be removed by cautious evaporation at a temperature below 100° F., but a large excess produces complete decomposition. To ascertain the quantity of water which in such case combines with the green powder, 2.820 grammes were very slightly moistened, and the excess of water removed by a temperature of 80°. The dry blue powder remaining weighed 3.605, or the green powder had taken 27.8 water per cent., corresponding to three equivalents, and hence the formula $NH_3 . CuO + SO_5$ becomes probably $(NH_3 . HO.)\, SO_3 + (CuO + 2HO)$.

By the results of the action of a large quantity of water on this green powder are formed sulphate of ammonia, the soluble ammoniacal sulphate of copper, and a bluish green basic sulphate not containing ammonia. In order to understand the reaction it was necessary to analyze this latter :

A. 3.710 grammes gave, dried, a brown powder 3.106, corresponding to 16.28 water per cent. ; this brown powder, dissolved in muriatic acid, and precipitated by chloride of barium, gave sulphate of barytes 1.766 grammes, corresponding to 16.36 of sulphuric acid per cent.

These proportions approximating to those of the common basic sulphate, another analysis was made with more complete accuracy :

B. 5.040 grammes of another specimen gave, dried, a brown powder 4.275, which, dissolved in muriatic acid, and precipitated by chloride of barium, gave 2.678 of sulphate of barytes ; hence the composition

		Theory.		Experiment.	
				A.	B.
SO_3	=	40.16	17.13	16.36	17.26
$4CuO$	=	158.40	67.52		
$4HO$	=	36.00	15.35	16.28	15.18
		234.56	100.00		

Thus the basic sulphate resulting from this reaction is the ordinary one, and the analyses given confirm the formula $SO_3 + 4CuO + 4HO$, which had been in some degree doubtful. The decomposition can be thus explained, the water being omitted for the sake of simplicity :

$$\begin{array}{lcr} 3(SO_3 . NH_3) & = & 3NH_3 + \qquad 3SO_3 \\ SO_3 + CuO + 2NH_3 & = & 2NH_3 + CuO + SO_3 \\ SO_3 + 4CuO & = & 4CuO + SO_3 \\ \hline 5(NH_3 . CuO)\,SO_3 & & 5NH_3 + 5CuO + 5SO_3 \end{array}$$

When this salt is heated it does not lose water until the temperature rises to above 300°, but then it loses all, and the brown powder, if exposed to the air, reabsorbs water slowly ; if moistened, it combines with the water rapidly, evolving heat, and regains its original proportion, and also its proper colour.

II. OF A NEW BASIC SULPHATE OF COPPER.

Having found, as in the preceding instance, that by the action of water on the ammoniacal compounds of the metals under examination, there was generated a series of basic salts, I became desirous of re-examining some of those already known, particularly in order to determine the function of the water which they constantly retain. For this purpose I prepared several portions of the sub-sulphate of copper, and I soon perceived, that, according to the quantity of alkali employed in the precipitation, where potash had been used, there were two distinct precipitates produced, the one of the bluish green generally described, the other of a clear grass green, resembling that of hydrated oxide of nickel. When ammonia was employed, the former alone was produced, and the formation of the latter I found to occur where the whole of the copper had been thrown down, but the liquor had not yet begun to react alkaline. It is singular that this basic sulphate had not been observed by any of those chemists who examined the common species. I found it in the first instance accidentally, but I have since seldom failed in preparing it completely pure.

It was analyzed as follows:

A. 7.124 grammes were dried until all traces of watery vapour ceased; there remained a brown powder 5.614, or 78.8 per cent. This was dissolved in muriatic acid, and precipitated by chloride of barium; there was obtained 1.851 of sulphate of barytes, indicating of sulphuric acid 8.94 in 100 of green powder.

B. 3.877 grammes were exposed to a temperature of 300° F. in an oil-bath, until it ceased to give off water, it then weighed 3.460. The oil-bath having been removed, the drying was completed by the spirit-lamp, at a temperature of about 500°, after which there remained 3.042. There had been thus driven off:

In first period	=	10.76 per cent.
In second period	=	10.52
Water in 100 of powder	=	21.28

The composition resulting is:

		Theory.		Experiment.	
				A.	B.
SO_3	=	40.16	8.83	8.94	
$8CuO$	=	316.80	68.00		
$12HO$	=	108.00	23.17	21.20	21.28
		464.96	100.00		

When the brown mass resulting from the desiccation of this salt is moistened, it evolves much heat, and combines with a large quantity of water, forming a green mass of a livelier colour than it originally possessed, and becoming always of something more than its former weight. The quantity of water with which it combines varies from 23 to 24 per cent., and hence I attribute the slight deficiency in water shown by analysis, to some of the chemically combined water having been expelled by the very moderate heat applied in drying the precipitate for analysis.

It will be remarked that by 300° F. exactly half of the water is expelled; hence there must be some difference in the degrees of affinity with which the two quantities are retained. From these considerations I am disposed to give to the formulæ for these basic sulphates the following form:

$$CuO \,.\, SO_3 \,.\, CuO + 6(CuO + 2HO),$$

or

$$CuO \,.\, SO_3 \,.\, CuO + 6CuO + 6HO + 6HO\,;$$

the second group of equivalents of water being expelled by a temperature lower than that necessary for the separation of the remainder.

Thompson had long since pointed out the existence of a basic sulphate of copper containing two equivalents of oxide, and this in its hydrated condition he states to retain two equivalents of water. When this is added to those above described, the series of basic salts follow from the neutral sulphate in the following order:

Real neutral sulphate = $Cu.O + SO_3$
Do. with saline water = $CuO \,.\, HO + SO_3$
First basic salt, dry = $CuO \,.\, CuO + SO_3$
Do. do. hydrated = $CuO \,.\, CuO + SO_3 + 2HO$.

Second basic salt, dry = $(\mathrm{c}u\mathrm{o} \,.\, \mathrm{c}u\mathrm{o})\,\mathrm{so}_3 + 2\,\mathrm{c}u\mathrm{o}$
Do. do. hydrated = $(\mathrm{c}u\mathrm{o} \,.\, \mathrm{c}u\mathrm{o})\,\mathrm{so}_3 + 2\,\mathrm{c}u\mathrm{o} + 4\,\mathrm{HO}$
Third basic salt, dry = $(\mathrm{c}u\mathrm{o} \,.\, \mathrm{c}u\mathrm{o})\,\mathrm{so}_3 + 2\,\mathrm{c}u\mathrm{o} + 4\,\mathrm{c}u\mathrm{o}$
Do. do. hydrated = $(\mathrm{c}u\mathrm{o} \,.\, \mathrm{c}u\mathrm{o})\,\mathrm{so}_3 + 2\,\mathrm{c}u\mathrm{o} + 4\,\mathrm{c}u\mathrm{o} + 6\,\mathrm{HO} + 6\,\mathrm{HO}$

III. OF THE AMMONIACAL CHLORIDE OF COPPER, AND OF THE COMPOUNDS DERIVED FROM IT.

When water of ammonia is added to a solution of chloride of copper, the precipitate which is at first formed redissolves by an excess, and a purple liquid is produced. If this be evaporated there is deposited a bluish flocculent precipitate, and the liquid loses its fine purple colour, and becomes bluish green. If in this condition the solution be set aside to crystallize, the double chloride of copper and ammonium is deposited, which Henry and Cap* have mistaken for the ammonia-chloride, and they have consequently assigned to the latter body a constitution belonging to one of a totally different nature, and which had resulted from its decomposition.

In order to obtain the ammonia-chloride pure and crystallized, a solution of chloride of copper must be taken, nearly saturated when hot, and a stream of ammoniacal gas passed through it, until the precipitate which first appears has been totally redissolved: the mass is kept almost boiling by the heat evolved in the condensation of the ammoniacal gas, and when set aside to cool, the ammonia chloride is deposited in small, but well-marked, octohedrons, or square prisms with pyramidal summits, of a deep blue colour. These crystals must be dried with great care between folds of filtering paper, without the aid of heat, and in a room free from any acid fumes; even with the greatest caution it is difficult to prevent the outer portion of the mass from acquiring a green tinge, arising from loss of ammonia, which will affect in a corresponding degree the analytical results.

Although the existence of this body had been generally admitted by chemists, yet no analysis of it had appeared until that by Henry and Cap; and as it is necessary to disprove their erroneous statement, I will detail those which I performed.

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* Journal de Pharmacie, December, 1837.

A. 5.823 grammes of crystals, slightly tarnished, were dissolved in dilute muriatic acid, and treated by sulphuretted hydrogen, until the copper was completely thrown down. The sulphuret of copper was then separated by the filter, and the liquid, with the washings, evaporated in a water-bath. There were obtained 5.211 of sal ammoniac, corresponding to 89.49 per cent., containing 28.83 of ammonia.

B. 4.700 grammes of crystals, dissolved in muriatic acid, and precipitated by caustic potash in excess, gave oxide of copper 1.692, or 36 per cent., containing 28.73 per cent. of copper.

C. 3.594 grammes of crystals were dissolved in an excess of pure nitric acid, and precipitated by nitrate of silver; the chloride of silver formed, collected, well washed, dried, and fused, weighed 4.672, or 130.5 per cent., containing 32.19 chlorine.

Hence there is the formula $cucl + 2NH_3 + HO$, giving

		Theory.			Experiment.
cl	=	35.42	32.11		32.19
cu	=	31.60	28.65		28.73
$2NH_3$	=	34.28	31.08		28.83
HO	=	9.00	8.16	and loss	10.25
		110.30	100.00		100.00

There occurred here a loss of ammonia, which evidently arose from the surface of the crystals having become a little tarnished, and likewise from that which takes place in all evaporations of ammoniacal solutions. Nevertheless, the theoretical and experimental results agree so closely, that there cannot be any doubt of the truth of the formula adopted; it resembles in every respect that of the ammonia-sulphate, and in accordance with the principles explained in the description of that substance, I consider the chlorine to exist in the crystals as sal ammoniac, and the rational formula to be

$$NH_3 . Hcl + cuO.NH_3.$$

When these crystals are exposed to heat, they melt, and ammonia, with watery vapour, is disengaged; I could not succeed in eliminating water without losing ammonia at the same time; in that respect therefore it resembles the ammonia-sulphate. By a temperature of 300° all the oxygen is separated as water, together with one-half of the ammonia, and there remains a fine apple-green powder, resembling very much that from the sulphate, and containing the remainder of the ammonia, with all the chlorine and the copper. Thus, 4.064 of the crystals were heated in an oil-bath, until the disengagement of water and ammonia had ceased; the green powder remaining weighed 3.109, or 76.5 per cent. According to theory, the residue $cl.cu.NH_3$ should weigh 76.3 per cent.; $OH.NH_3$ having been expelled. When this body $cl.cuNH_3$ is exposed to a higher temperature it is decomposed, sal ammoniac sublimes, and sub-chloride of copper remains; there are likewise azote and ammonia given off. The ammonia is retained by so powerful an affinity, that it cannot be expelled by any temperature, without the substance being totally decomposed.

The existence of this body was noticed by Graham, as resulting from the absorption of ammonia by chloride of copper at a high temperature. At ordinary temperatures chloride of copper absorbs three equivalents of ammonia, of which two are easily expelled, but the third is retained more powerfully, and constitutes with the chloride the body just described. We may therefore consider the ammonia-chlorides, formed by water, and by dry ammonia, as corresponding compounds; thus,

$$NH_3\,cu\,cl + NH_3 .\ HO.$$
$$NH_3\,cu\,cl + NH_3 .\ NH_3 ;$$

an equivalent of water in the one replacing an equivalent of ammonia in the other, and both, when heated, giving the body $NH_3.cu.cl$, by losing respectively $NH_3.HO$ and $2NH_3$.

IV. OF A NEW BASIC CHLORIDE OF COPPER.

When the body $cl.cuNH_3$ is treated by water it is decomposed; there is dissolved the ammonia-chloride of copper just described, and a quantity of sal ammoniac, and a bluish green powder remains, insoluble in water, and not containing ammonia. When heated it gives off water, and becomes brown; but exposed to the air, it gradually regains a certain quantity of water. Its analysis was effected as follows:

A. 1.901 grammes, dried over a spirit-lamp, gave a chocolate brown powder, which weighed 1.522 grammes, corresponding to 80.06 per cent. This 1.522

were dissolved in nitric acid, and precipitated by nitrate of silver. The chloride of silver produced weighed 0.964, or 50.71 per cent. for the green powder, and containing 12.51 of chlorine.

B. 2.678 grammes, dried over the spirit-lamp, gave, of brown powder, 2.143 or 80.02 per cent., which was boiled in a strong solution of caustic potash, and the oxide of copper washed, until the liquors were perfectly free from traces of free alkali; there was obtained 1.891 of oxide of copper, or 70.61 in 100 of green powder, and containing 56.31 of metal.

Hence the formula $cucl + 4cuo + 6\mathrm{HO}$ results, which gives

	Theory.		Experiment. A.	Experiment. B.
cl =	35.42	12.68	12.51	
$5cu$ =	158.00	56.55		56.31
$4\mathrm{O}$ =	32.00	11.45		
$6\mathrm{HO}$ =	54.00	19.32	19.94	19.98
	279.42	100.00		

$$\left.\begin{array}{l} cucl + 4\,cuo \\ 4\,cl\mathrm{H} + 4\,\mathrm{NH}_3 \\ cucl + 2\,\mathrm{NH}_3 \end{array}\right\} = 6.cucl.\mathrm{NH}_3 + 4.\mathrm{HO}.$$

The coincidence is quite satisfactory.

This oxychloride differs therefore from that analyzed by Berzelius, in containing, to the same quantity of chloride of copper, one atom more of oxide of copper, and two more of water. The relation between this and the ordinary oxychloride, can be very well shown, by arranging the formulæ of the two in the following manner:

Common oxychloride $= cucl.\,cuo + 2(cuo + 2\,\mathrm{HO})$
New oxychloride $= cucl.\,cuo + 3(cuo + 2\,\mathrm{HO})$

V. OF A SECOND NEW BASIC CHLORIDE OF COPPER.

Having prepared, during the course of these researches, a great number of specimens of Brunswick green, I remarked that some, which had been produced by a less perfect precipitation by the alkali employed, were of a much less brilliant colour, and differed markedly in their aspect from the ordinary oxychloride. I consequently submitted these specimens to an examination, from which it results, that there may be prepared, by the action of a base on an excess of solution of chloride of copper, two oxychlorides; that generally formed being the common Brunswick green, with the formula $cu\,cl + 3\,cu\,o + 4\,\mathrm{HO}$, but that when a still smaller quantity of base is employed a different substance is produced.

This new oxychloride resembles remarkably in its aspect that last noticed and the sub-sulphate, but can be at once distinguished from Brunswick green by its pale colour; heated it gives out water, and becomes first brown, and leaves finally a black powder. When this powder is moistened it slakes, evolving great heat, and becoming of a very brilliant green colour, brighter than that of Brunswick green. By heat the water reabsorbed may be again expelled, and so repeatedly, without total decomposition taking place.

The analysis of this oxychloride was conducted in the following manner:

A. 12.390 grammes, dried over the spirit-lamp, gave a black powder, weighing 9.725, or 78.49 per cent. These 9.725 were moistened with water, and allowed to assume throughout the rich green colour; the excess of water, which was very slight, was removed by a temperature of 100° F., when the green powder was found to weigh 11.670, having absorbed 16.78 per cent. of water.

B. 5.155 grammes of the green powder, thus formed, were kept at a temperature of 280°, until it ceased to give out watery vapour; it had become chocolate brown, and weighed 4.584. It had lost therefore 11.08 per cent. of the water which it contained.

C. 6.185 grammes of the same green powder, dried at 500° F, gave 5.144 of black powder, or 83.17 per cent.; hence it had lost 16.83 water.

D. The 4.584 of B was dissolved in dilute nitric acid, and precipitated by nitrate of silver, the chloride was collected, washed, and dried, it then weighed 4.099, corresponding to 79.51 per cent., and containing 20.61 of chlorine in the bright green condition.

E. The 5.144 of C was dissolved in dilute muriatic acid, and treated with boiling solution of potash, the oxide of copper which separated was well washed, and collected on a filter, and subsequently ignited. There was obtained 4.112, corresponding to 79.93 per cent., and containing 63.78 of copper.

It consequently follows, that the dry oxychloride is capable of uniting with water in three different proportions; thus,

In pale green powder	100	oxychloride take	27.4	water.
In bright green do.	100	do.	20.2	
In brown do.	100	do.	6.9	

But 6.9, 20.2, and 27.4 are nearly as 1, 3, and 4.

From C, D, and E it results, that the dry oxychloride has the composition

		Theory.		Experiment.
cl	=	35.42	24.22	23.59
$3cu$	=	94.80	64.84	63.78
$2o$	=	16.00	10.94	10.77
		146.22	100.00	98.14

From the proportion of water, it is evident that the dry oxychloride combines with one, three, and four equivalents in the three different conditions in which it exists, and that hence there are the formulæ

1. $cucl + 2cuo.$
2. $cucl + 2cuo + \mathrm{HO}.$
3. $cucl + 2cuo + 3\mathrm{HO}.$
4. $cucl + 2cuo + 4\mathrm{HO}.$

The discovery of this body leads us to some very interesting relations, in this class of substances; thus, this one is evidently the simplest oxychloride, being related to the crystallized hydrated chloride, as

$$cucl + 2cuo \text{ to } cucl + 2\mathrm{HO};$$

and the first atom of water being so strongly retained, points out the passage through

$$cucl + \mathrm{HO} + 2cuo$$

to

$$cucl + cuo + 2cuo,$$

the ordinary oxychloride deprived of water, but both combining with additional quantities of water, and acquiring the brilliant green colour by which they are respectively characterized; and the condition in which this salt retains most water, gives to it a composition which brings to mind the crystallized hydrates of many chlorides of the same class, as

$$cucl + 2cuo + 4HO.$$

compared with

$$ca.cl + 2HO + 4HO.$$

and

$$Mgcl + 2HO + 4HO.$$

I will have occasion to recur to these bodies when speaking of their analogues among the compounds of zinc.

The other new oxychloride of copper, in its dry condition, is analogous to the chlorides which crystallize with four atoms of water, as iron and manganese.

When this oxychloride, in a dry condition, is exposed to a current of ammoniacal gas, an absorption takes place, with the evolution of some heat; but although the current may be continued long after the mass shall have become cold, yet no alteration of colour occurs, the mass remaining brown. If the ammonia be passed over the oxychloride in its hydrated condition, it becomes blue, water is given out, and the whole is evidently decomposed; and if the brown mass be wetted, there is formed a hydrated oxychloride and a blue liquor, showing total decomposition.

Dry ammonia, acting on dry oxychloride, gave the following results:

I. 4.801 of oxychloride absorbed 0.504 ammonia, or 10.4 per cent.

II. 3.970 of oxychloride absorbed 0.436 ammonia, or 11.1 per cent.

These numbers give, for the proportion absorbed, almost exactly one equivalent; and the resulting brown mass has evidently the formula

$$cucl + 2cuo + NH_3.$$

According to which 100 should have absorbed 11.8 of ammoniacal gas.

Now putting $NH_3 = HAd$, the relation of this body with those last noticed becomes very remarkable, as we must contemplate the series

$$\begin{array}{l} cucl + 2cuo + cuo \\ cucl + 2cuo + HO \\ cucl + 2cuo + HAd. \end{array}$$

in which cu and H, O and Ad mutually replace each other.

VI. OF THE AMMONIA-OXIDE OF COPPER.

I had examined very frequently, and under a great variety of circumstances, the precipitates which are produced by the action of ammonia on solutions of the sulphate, nitrate, and chloride of copper, in order to determine whether compounds similar to those generated under like circumstances with solutions of the quicksilver salts, could be produced. In all such cases, I found the precipitates to be basic salts following certain laws of composition, and not containing ammonia as an element. Indeed a similar result might have been anticipated from what has been already shown in this paper; namely, that the insoluble ammonia-copper compounds are all decomposed by water, giving soluble ammonia compounds and a basic salt destitute of ammonia in its composition.

However, on one occasion, on treating a solution of chloride of copper with ammonia, I obtained a precipitate of a remarkably fine blue colour, approximating to that of the hydrated oxide, or of the refiner's verditer. In the one operation I obtained a sufficient quantity of it for examination, and did not since study the exact circumstances favourable to its production, the specimen I had procured being sufficient to supply my wants, but proceeded at once to determine its properties and composition.

This blue powder is not affected by repeated washings, to which I subjected it, suspecting that its ammoniacal constituent might result from sal ammoniac being attached. It may be heated to 300° F. without being changed, but above that temperature it is rapidly decomposed with a hissing noise. It yields much ammonia, azote, and a large quantity of water, and the residue is red coloured, consisting of a mixture of sub-oxide of copper and of copper in the metallic state. There is no sublimate of sal ammoniac.

Dissolved in dilute nitric acid, this powder gives no precipitate with nitrate of silver. Its elements are therefore ammonia, water, and oxide of copper. The following quantitative analysis was made:

A. 3.410 grammes were dissolved in muriatic acid, and the solution decomposed by sulphuretted hydrogen. The sulphuret of copper having been removed, the liquor and washings were evaporated to perfect dryness in a water-bath, and sal ammoniac, weighing 1.634, was obtained, corresponding to 15.70 per cent. of ammonia.

B. 3.752 grammes were dissolved in dilute muriatic acid, and decomposed by boiling with caustic potash. The oxide of copper precipitated was collected and burned with the filter, it weighed 2.146 or 57.19 per cent.

The difference is evidently the water, and hence the formula

$$3\mathit{cu}O + 2NH_3 + 6HO,$$

which gives

		Theory.		Experiment.
$3\mathit{cu}O$	=	118.80	57.37	57.19
$2NH_3$	=	34.28	16.55	15.70
$6HO$	=	54.00	26.08	27.11
		207.08	100.00	100.00

This result comes sufficiently close to allow of the formula being adopted, but I will not now attempt to arrange it after any theoretical idea. The substance evidently belongs to the same class as the fulminating oxides of silver and mercury, but is still inferior in detonating power even to the latter.

VII. OF THE AMMONIACAL NITRATE OF COPPER.

This salt, the existence and some characters of which have been already noticed by chemists, may be prepared very simply by the same process as that described under the head of the Ammonia-Chloride of Copper, substituting nitrate for the chloride. It crystallizes in a confused mass of minute octohedrons, whose form is with difficulty ascertained. It dissolves easily in water, and on the addition of an acid it yields the ordinary basic nitrate of copper.

When heated, this salt is decomposed in a very remarkable manner: traces of ammonia are evolved, but no water if the salt had been completely dried; black points (oxide of copper) make their appearance, the salt fuses, and if the heat be continued, suddenly explodes with a hissing noise, and the formation of a great cloud of gaseous matter, whilst the inside of the vessel remains lined with oxide of copper. Several attempts were made to manage the decomposition, so as to determine the quantity of the oxide left behind, but without avail; even when the powdered salt was covered in a platinum crucible, with strong nitric or muriatic acid, and then heated, the acid boiled away, and the residual salt underwent its explosive change, as if no such means had been applied.

No quantitative analysis of this body has been recorded, and as from the remarkable circumstances of its decomposition by heat, it is of great importance that its composition should be accurately known, the following analysis was made:

5.982 grammes were introduced into a globe with a strong solution of potash; from this globe there passed a bent tube, dipping into a tall jar containing water with muriatic acid. The mass in the globe was boiled until all the ammonia had been set free, and more than one-half of the liquor had distilled over. The fluid in the jar was then carefully evaporated in a water-bath to dryness, and the sal ammoniac obtained was found to weigh 4.717 or 78.85 per cent., containing 25.23 of ammonia.

The liquor remaining in the globe was diluted with water, and, when cold, filtered; the oxide of copper remaining weighed 1.856 grammes, corresponding to 31.03 per cent.

These numbers give the formula $cuO.NO_5 + 2NH_3$, by which there should have been obtained

	Theory.		Experiment.
cuO =	39.60	30.94	31.03
NO_5 =	54.14	42.28	
$2NH_3$ =	34.28	26.78	25.23
	128.02	100.00	

Since during the process for the formation of the ammonia-nitrate, the first stage consists in the production of the ordinary subnitrate of copper, the nitric acid in the ultimate product must unavoidably be considered as united with ammonia, and hence the above empirical formula must, in assuming a rational form, become

$$(NH_3.HO)\,NO_5 + cuNH_2,$$

from which it follows, that the copper in this compound is united with amidogene.

It is now easy to explain the various circumstances in which this body differs from the similarly constituted ammonia-chloride and sulphate just described. By the application of heat, the evolution of ammonia and water cannot occur, since the second group $cuNH_2$ is not of a nature precisely to replace it. The trace of ammonia which is evolved arising probably from a partial expulsion of HNH_2 by $cuNH_2$. The salt resists decomposition almost completely, until the nitrate of ammonium melts, and commences to be decomposed, when the sudden burning of the amidogene and copper, in the oxygen of the nitrous oxide formed, gives rise to the explosive reaction which distinguishes this body.

In order to place in a still clearer point of view the peculiar nature of this body, I shall refer briefly to some observations which I have made on the ammonia-nitrate of silver discovered by George Mitscherlich. On analyzing it he obtained the formula $NO_5 + AgO + 2NH_3$, and I have verified his result, having obtained from it 52.46 of silver, whilst his formula indicates 52.83. This formula is evidently quite similar to that given by the ammonia-nitrate of copper; and here also the action of the ammonia consists in the separation of the oxide of silver in the first stage and its solution afterwards, when the ammonia has been added in excess. Giving to the formula, therefore, its true rational construction, it becomes

$$(NH_3 . HO)\, NO_5 + AgNH_2,$$

and the propriety of this view is supported by a very curious reaction of this body, which George Mitscherlich does not appear to have observed.

When heated this salt fuses very readily, and gives out a mixture of azote and ammonia, whilst silver is separated in the metallic form, and by rolling about the fused mass in the tube, a mirror surface is produced, as beautiful as that obtained by nitrate of silver with ammonia-aldehyd. When the tube cools, the melted mass solidifies, and is found to be nitrate of ammonia. This I consider to be a convincing proof of the existence of an amidide of silver in this salt; its easy reduction, the simultaneous liberation of the elements of amidogene, and the nitrate of ammonium being set free, unaltered, if the heat be not raised too high, render the peculiar nature of this body too remarkable to be mistaken. Now in the analogous copper compound, the amidide of copper is not so easily decomposed, its elements remain united until the nitrate of ammonium begins to yield, and then a rapid combustion, alike of copper and amidogene, takes place in the oxygen of the nitrous oxide formed.

Although the ammonia-copper element of the ammonia-sulphate of copper cannot be freed from water, yet in the silver salts, the ammonia-sulphate, and its congeners, which, in the hands of Eilard Mitscherlich, have become one of the most beautiful instances of isomorphism, crystallize without that equivalent of water, and the empirical formulæ

$$\begin{array}{l} SO_3 + AgO + 2NH_3 \\ CrO_3 + AgO + 2NH_3 \\ SeO_3 + AgO + 2NH_3 \end{array}$$

assume from the above principles the form

$$\left.\begin{array}{l} SO_3 \\ CrO_3 \\ SeO_3 \end{array}\right\} + NH_3 . HO + AgNH_2 .$$

Of these I have re-examined only the sulphate, and that without observing any fact new in its history.

When chloride of silver is dissolved in water of ammonia, rhomboidal tables are produced, white and opaque, consisting of an ammonia-chloride ; they lose ammonia, however, immediately on being removed from the solution, and hence their quantitative analysis became impossible.

VIII. OF THE AMMONIA-CHLORIDE OF ZINC.

When water of ammonia is added to a solution of chloride of zinc, the white precipitate of basic chloride which is at first produced, soon redissolves, and a colourless liquor is obtained, from which, by evaporation at a moderate temperature, crystals may be obtained. These crystals, however, according to circumstances, present very different appearances, and possess quite different properties and composition, and hence the proper methods of obtaining each variety, in a state fit for accurate examination, must be noticed. The plan which I found most successful was to take a strong and hot solution of chloride of zinc in water, to pass into it a stream of gaseous ammonia, until the precipitate was completely redissolved, and filtering very rapidly, in order to separate any traces which might yet remain of turbidity from undissolved material, to allow the whole to cool. A substance, in very minute, but brilliant plates, of a peculiarly soft and talcy feel, and pearly lustre, is deposited, while the liquor cools ; but after it has cooled, then by further evaporation a completely different salt is formed, which crystallizes in stellated groups of square prisms of a brilliant vitreous lustre, and hard to the feel. These two salts I shall indicate as the tabular and the prismatic ammonia-chlorides.

To analyze the tabular ammonia-chloride of zinc, the following method was employed:

A. 3.374 grammes were dissolved in dilute nitric acid, and precipitated by nitrate of silver added in excess; the chloride of silver formed was collected, carefully washed, and dried; it weighed 4.295 grammes, equivalent to 127.3 per cent., containing 31.40 per cent. of chlorine.

From the circumstances of the preparation of this substance, it necessarily follows, that, as in the corresponding copper-salt, the number of atoms of metal is equal to, and that of the ammonia double that of the chlorine; hence the above determination of the chlorine was fully sufficient to determine the composition of the whole. Thus the formula $zncl + 2NH_3 + HO$ gives

		Theory.		Experiment.
zn	=	32.30	29.10	
cl	=	35.42	31.89	31.40
$2NH_3$	=	34.28	30.90	
HO	=	9.00	8.11	
		111.00	100.00	

Thus the composition of this body corresponds in every particular to that of the ammonia-chloride of copper; and guided by similar considerations, I shall arrange its constituents according to theory, as

$$NH_3 . HCl + NH_3 . znO.$$

When this body is heated it gives out water and ammonia, and the result obtained confirms fully the analytical result above described. Thus,

3.739 of this tabular ammonia-chloride, heated to 300°, until all evolution of ammonia and of water had ceased, left a white powder, weighing 2.900, or 77.56 per cent.

In another experiment, 4.457 kept in a temperature of 300°, until the evolution of water and of ammonia had ceased, left 3.426 of white matter, corresponding to 76.87 per cent. But from theory there should be, supposing the reaction similar to what has been observed in the copper series,

$zncl$	= 60.99	and	NH_3	= 15.45
NH_3	= 15.45		HO	= 8.11
	76.44			23.56

By the loss of NH_3HO there is produced the substance $NH_3 . zncl$, which remains behind. When this powder is farther heated it fuses into a clear colourless, or very slightly yellow liquid, emitting ammonia; by cooling, this matter congeals into a mass like gum; it shall be examined more minutely a little farther on.

The form and external characters of the prismatic ammonia-chloride of zinc have been already given; its analysis was effected as follows:

A. 2.851 grammes were dissolved in dilute nitric acid, and precipitated by nitrate of silver; the chloride, collected, washed, and dried, weighed 4.550, or 160 per cent., containing 39.47 chlorine.

B. 3.540 grammes were dissolved in dilute muriatic acid, and precipitated by carbonate of soda; the precipitate was collected, and carefully washed, and having been dried, was ignited with its filter; the residual oxide of zinc, allowing for the ashes of the filter, weighed 1.573, or 44.43, containing 35.61 of metallic zinc.

Hence in this compound likewise, the zinc and chlorine are in the proportion of atom to atom; it contains likewise water and ammonia, and calculating from the formula $2(clzn) + 2NH_3 + HO$, there is found

	Theory.		Experiment.
$2cl$	= 70.84	39.64	39.47
$2zn$	= 64.60	36.14	35.61
$2NH_3$	= 34.28	19.18	24.92
HO	= 9.00	5.04	
	178.72	100.00	100.00

Thus this prismatic ammonia-chloride differs from the tabular salt in containing, united with the same quantity of ammonia and water, double the quantity of chloride of zinc, and it has evidently been produced by the dissipation during the evaporation of the liquors, of one-half of the ammonia and combined water which the tabular salt had contained. Hence the true nature of this salt may be best represented as a compound of chloride of zinc with the tabular salt, thus,

$$zn\mathrm{C}l + \mathrm{NH_3} . \mathrm{HC}l + \mathrm{NH_3}\, zn\mathrm{O},$$

and recollecting the frequent replacements of water of crystallization by $\mathrm{NH_3} = \mathrm{HA}d$, some remarkable relations present themselves, as

$$zn\mathrm{C}l + \mathrm{NH_3} . \mathrm{HC}l + \mathrm{HA}d\mathrm{HO},$$

$$zn\mathrm{C}l + \mathrm{NH_3} . \mathrm{HC}l + 2\mathrm{HO};$$

and again,

$$cu\mathrm{C}l + \mathrm{NH_3HC}l + 2\mathrm{HO}.$$

Hence this prismatic salt assimilates itself very remarkably to the double chlorides of zinc, copper, and ammonium, with water of crystallization; a view which is additionally strengthened by the effects of heat upon this body.

When this ammonia-chloride is heated it emits watery vapour and ammonia, and fuses into a transparent mass, which resists a considerable temperature. This residue, on cooling, forms a mass like pale amber, having but little or no traces of crystalline arrangement, but fissured in every direction like starred glass. To determine the proportion of water and ammonia lost in this reaction, the following experiments were made.

A. 3.250 grammes of prismatic ammonia-chloride gave 2.758 of transparent gummy-looking mass, corresponding to 84.81 per cent.

B. 12.435 grammes gave, similarly treated, 10.748, or 86.47 per cent.

From these results the nature of the substance remaining may be very simply calculated: all the water is driven off, and as much ammonia as may be necessary to account for the weight lost; hence, there result

$$\begin{array}{lcr} zn\mathrm{C}l & = & 75.78 \\ \mathrm{NH_3} & = & 9.59 \\ \hline & & 85.37 \end{array} \quad \text{and} \quad \begin{array}{lcr} \mathrm{NH_3} & = & 9.59 \\ \mathrm{HO} & = & 5.04 \\ \hline & & 14.63 \end{array}$$

Hence it is evident that precisely the half of the ammonia is driven off with all the water, forming the elements of oxide of ammonium, and there remains the remainder of the ammonia, with the chloride of zinc, thus arranged:

$$zn\mathrm{C}l + (\mathrm{NH_3} . zn\,\mathrm{C}l;)$$

wherein the body $\mathrm{NH_3} . zn\mathrm{C}l$, already noticed, is united with chloride of zinc, constituting an anhydrous double chloride, analogous to that of zinc and of ammonium or potassium.

When the body $NH_3 . zncl$ is heated by itself, it gradually loses ammonia, and fuses into the same gummy-looking substance; but the numerical results being similar to those already noticed, it is not necessary to occupy space with them, the more so, as the elimination of the ammonia, by itself, does not take place so clearly as where the portion to be separated is associated with the equivalent quantity of water.

This gummy body, when heated strongly, nearly to redness, boils, but does not emit ammonia; on the contrary, it volatilizes unchanged, and condenses in amber-looking drops, possessing all its original characters. If it be heated, however, with dry lime, there is an immediate and copious evolution of ammonia; when treated by water it is decomposed; there dissolves ammonia-chloride, probably in the prismatic form, and a white powder remains, which is an oxychloride of very remarkable constitution. The same oxychloride is produced by the action of water on the white powder $NH_3 . zncl$, and I shall consequently treat of the properties and composition of this oxychloride without further reference to which of these ammonia zinc-chlorides it had been obtained from.

IX. OF THE OXYCHLORIDE OF ZINC OBTAINED BY THE ACTION OF WATER ON $NH_3 zncl$ or $NH_3 + 2zncl$.

The substance thus obtained is a very light milk-white powder, tasteless, and insoluble in water; when heated it gives out water, and if ignited, it yields some vapours of chloride of zinc, and is completely decomposed; water subsequently poured upon it, extracting some of the chloride of zinc, and leaving a still more basic combination. The quantity of water which this oxychloride retains is very variable, as a very slight difference in the temperature used in drying it may change, very considerably, the proportion of water with which it may be combined. A quantity prepared by acting with water on $NH_3 . zncl$, and dried at a temperature of about 180° F., gave the following result:

A. 2.404 grammes, dried, until all escape of watery vapour had ceased, gave 2.043 of residue, which had a greyish shade. These 2.043 were dissolved in dilute nitric acid, and precipitated by nitrate of silver; the chloride of silver, collected and dried, weighed 0.975, being 40.56 per cent., containing 10.01 of chlorine.

The quantity of water lost was 0.361, corresponding to 15.02 per cent.

But the chlorine being as chloride of zinc, and the remainder of the deficiency being oxide of zinc, the composition of the whole may be easily calculated, and there is found

$$\begin{aligned} cl.10.01 + zn\ \ 9.13 &= 19.14 = zncl \\ \mathrm{O}.13.07 + zn\,52.77 &= 65.84 = zno \\ &\ 15.02 = \mathrm{HO} \\ &\overline{\ 100.00} \end{aligned}$$

But $\frac{52.77}{9.13} = 5.78$. q. p. 6. And $\frac{10}{15} = \frac{35.42}{53.2}$, or $6\mathrm{HO}$. Hence the empirical formula is $zncl + 6zno + 6\mathrm{HO}$.

When this oxychloride is dried at the temperature of the air, it retains a much larger quantity of water, in fact nearly double as much, since quantities of the powder so prepared, gave, when dried, from 23.5 to 23 per cent. of water To establish an accurate proportion, however, the following analysis was made :

B. 2.078 of the oxychloride, prepared by the action of water on the body $\mathrm{NH}_3.zncl$, and dried without exposure to heat, gave, when dried by the spirit-lamp, 1.590 of a greyish residue, corresponding to 76.51 per cent.; hence 23.49 water.

The residue was dissolved in nitric acid, and precipitated by nitrate of silver; the chloride of silver produced was collected, washed, and dried, when it weighed 0.690, or 33.21 per cent., containing 8.29 per cent. of chlorine.

The zinc being determined in the same manner as that before described, there results that to the same chloride and oxide of zinc, there were in this body united ten atoms of water in place of six; and hence the formulæ of these oxychlorides are :

		Dried at 212°.		Experiment.
cl	=	35.42	9 74	10.01
$7zn$	=	226.10	62.20	
$6\mathrm{O}$	=	48.00	13.20	
$6\mathrm{HO}$	=	54.00	14.86	15.02
		363.52	100.00	

Dried in the open Air.			Experiment.
cl =	35.42	8.86	8.29
$7\,zn$ =	226.10	56.59	
$6\,o$ =	48.00	12.01	
$10\,HO$ =	90.00	22.54	23.49
	399.52	100.00	

When this oxychloride, dried, but not too much heated, has been exposed to the air, 100 parts of it gradually absorb about 15 of water, corresponding to four equivalents, and which cannot be expelled by the temperature of boiling water. It therefore appears to form in this proportion likewise a hydrate of definite composition.

When a solution of chloride of zinc is decomposed by ammonia, added in such excess as that part of the precipitate at first formed shall be redissolved, there is a hydrated oxychloride produced, which I have found to be in all respects identical with that just described. It has the same amylaceous look and feel, the same lightness, and, as shall be now shown, the same composition.

C. 4.60 grammes of this oxychloride, dried merely at ordinary temperatures, were heated over a spirit-lamp, until all evolution of watery vapour had ceased; there remained the greyish dry oxychloride, weighing 3.510, corresponding to 76.3 per cent., or 23.7 of water. The 3.510 residue was dissolved in dilute muriatic acid, and precipitated by solution of carbonate of soda; the precipitate of carbonate of zinc was washed carefully and ignited, when it left a pure oxide of zinc, weighing 3.237, or 70.22 per cent., containing 56.28 of metallic zinc.

D. A quantity taken from the same filter, was dried at 212°: it had the same appearance as the former. Of this 3.165 dried, left 2.690 of residue, giving 85.0 per cent. and 15.0 of water. The residue was dissolved in dilute nitric acid, and precipitated by nitrate of silver; the chloride formed, collected, and fused, weighed 1.223, or 38.64 per cent., containing 9.53 of chlorine. Hence this oxychloride was composed of

Dried at 60°.		Dried at 212°.	
cl =		cl =	9.53
zn =	56.28		
HO =	23.70	HO =	15.00

Which agree with the results of the theoretical formulæ given for the oxychloride last examined. When the ammonia employed is not sufficient to precipitate all the zinc, the oxychloride formed is differently constituted from that just described, and is the same with that described by Schindler, and which is analogous to the ordinary oxychloride of copper. Schindler, however, appears to have dried the specimens which he analyzed at 212°, for I have found this oxychloride to retain four equivalents of water at 100° F. Its formula is then

$$zncl + 3\,zno + 4\,\mathrm{HO}.$$

As the same result, except in the estimate of the water, had been obtained by Schindler, I will not enter into any details of my verifications of his results. I have, however, obtained another oxychloride, which, in a less hydrated condition, had been noticed by Schindler likewise. I prepared it by adding to a solution of chloride of zinc, caustic potash liquor, until it began to react alkaline. The process by which Schindler had obtained it, almost necessarily produced the separation of the water it should contain; thus he evaporated chloride of zinc until it had lost a certain proportion of muriatic acid, and then diluted with much water the remaining sirupy liquor. The formula which he obtained was

$$zncl + 9\,zno + 3\,\mathrm{HO}.$$

This oxychloride, as formed in my experiments, scarcely differs from those already described, in its external appearance; when heated it yields water in the same manner. The analysis of it merely, therefore, need be given in detail.

A. 1.790 grammes, dried over the spirit-lamp, gave 1.384 of residue, or 77.32 per cent.

B. 2.131, treated in the same manner, gave 1.646, or 77.24 per cent.

C. The 1.384 of residue, exposed to the air, gradually absorbed water, and became 1.485; therefore the quantity of water absorbed was to the original quantity as 101 to 406, or nearly as one to four.

D. 3.030 of dried oxychloride were dissolved in dilute nitric acid, and precipitated by nitrate of silver; the chloride produced weighed 0.938 grammes, or 30.96 per cent., equivalent to 23.93 per cent. for the hydrated oxychloride, which contains 5.921 of chlorine.

Hence is derived the formula $zncl + 9\,zno + 14\,\mathrm{HO}$, by which there should be

		Theory		Experiment.	
cl	=	35.42	6.37	5.92	
$10\,zn$	=	323.00	58.11		
$9\,o$	=	72.00	12.95		
$14\,HO$	=	126.00	22.67	22.68	22.76
		556.42	100.00		

And the dry oxychloride, $zncl + 9zo$, absorbs four equivalents of water, assuming nearly the condition in which it had been examined by Schindler. The quantity of water found by analysis is intermediate between three and four atoms, but I consider that the method used was most likely to lead to an error by deficiency of absorption than by excess, and hence I adopt four as the quantity re-absorbed. Then there is given the formula $zncl + 9zno + 4\,HO$.

There are thus found to exist at least three different oxychlorides of zinc, each of which may be obtained combined with various proportions of water.

In order to be able to trace the connexion between these oxychlorides, and to ascertain the relation in which they stand to the hydrated neutral chlorides of the same family, they may be arranged in the following manner:

$$\text{A.}\quad \left.\begin{array}{l} 1.\ zncl + zno + 2zno + 2\,HO \\ 2.\ zncl + zno + 2zno + 4\,HO \end{array}\right\} \begin{array}{l} \text{Hydrates of} \\ zncl + 3\,zno. \end{array}$$

$$\text{B.}\quad \left.\begin{array}{l} 1.\ zncl + 6zno + 4\,HO \\ 2.\ zncl + 6zno + 6\,HO \\ 3.\ zncl + 6zno + 10\,HO \end{array}\right\} \begin{array}{l} \text{Hydrates of} \\ zncl + 6zno. \end{array}$$

$$\text{C.}\quad \left.\begin{array}{l} 1.\ zncl + 9zno + 4\,HO \\ 2.\ zncl + 9zno + 14\,HO \end{array}\right\} \begin{array}{l} \text{Hydrates of} \\ zncl + 9zno. \end{array}$$

The oxychloride A and its hydrates conform to the type of the Brunswick green and of the oxychloride of mercury. Elsewhere the nature of this type will be discussed.

The oxychloride B, in its dry form, is evidently the basic compound corresponding to the chlorides, with six atoms of water of crystallization, and hence

$$zncl + 6zno$$

corresponds to

$$\mathrm{Mg}cl + 6\mathrm{HO}$$
$$ca.cl + 6\mathrm{HO}$$

and other cases, of which the chloride of hydrogen is the most remarkable.

When water is saturated with muriatic acid gas, the solution being kept at the temperature of 32° F., it acquires a specific gravity of 1.2109, and then contains in 100 parts 42.43 of gas, by Edmund Davy's determination. If the water be retained only at 60° the absorption does not proceed so far, the specific gravity reaching only about 1.192, and the liquor containing only 38.38 of chloride of hydrogen in the 100. Thompson found the strongest liquid acid to be 1.203, and to contain 40.66 per cent. of gas. Now, if we calculate the number of equivalents of water which these results indicate as combining with one of chloride of hydrogen, we shall find

In the acid of 1.2109 . $\frac{cl\mathrm{H}}{\mathrm{HO}} = \frac{36.42}{49.4}$ and $\frac{49.4}{9} = 5.5$

In the acid of 1.192 . $\frac{cl\mathrm{H}}{\mathrm{HO}} = \frac{36.42}{58.5}$ and $\frac{58.5}{9} = 6.5$

In the acid of 1.203 $\frac{cl\mathrm{H}}{\mathrm{HO}} = \frac{36.42}{53.15}$ and $\frac{53.15}{9} = 5.91$

Scarcely any doubt can remain, therefore, that in the strongest liquid muriatic acid, the chloride of hydrogen combines with six equivalents of water, and that it is hence analogous to

$$ca.cl + 6\mathrm{HO}$$

and to $zn\,cl + 6\,zno.$

This strong hydrated chloride of hydrogen cannot be heated without escape of gas, and if it be distilled, the boiling point gradually rises until it reaches 230° F. (110° C.) when it ceases to change, and the liquid subsequently distils unaltered. If a weaker acid be distilled, it loses water until the boiling point rises to the same degree, when acid of the same strength distils, as in the former instance. This acid, with a constant boiling point, has a specific gravity of 1.094, and contains 19.19 per cent. of real acid by Davy's estimate, and 20.44 by Thompson's; hence the proportion is, taking the mean of their results,

$$\frac{cl\mathrm{H}}{\mathrm{HO}} = \frac{19.82}{80.18} = \frac{36.42}{147.3} \text{ and } \frac{147.3}{9} = 16.35.$$

Hence this acid, with constant boiling point, is composed of $\text{HC}l + 16\text{HO}$, and its formula may properly be considered as

$$\text{H.c}l + 6\text{HO} + 10\text{HO}.$$

corresponding to

$$zncl + 6zno + 10\text{HO}.$$

the hydrated-oxychloride, which has been described.

X. OF THE AMMONIA-SULPHATES OF ZINC.

This salt was prepared by passing ammoniacal gas through a strong and hot solution of sulphate of zinc, until the whole of the sub-sulphate precipitated had been redissolved. The liquor, on cooling, deposited a flocculent mass, in semicrystalline grains resembling starch; and if the liquor be evaporated, or kept hot, the separation of this substance continues; when, however, the solution is allowed to cool, and then having been filtered, is left to spontaneous evaporation, it remains clear; and small, but perfectly distinct crystals are deposited, which remain bright while moist, but effloresce, and become opaque almost immediately on being dried and left in the open air. These two bodies contain alike, sulphuric acid, oxide of zinc, ammonia, and water, but the quantity of the constituents is not the same; I shall therefore describe them separately, commencing with the crystallized ammonia sulphate.

When this salt is heated it gives water and ammonia, and there remains sulphate of zinc; if the heat be very gently applied, all ammonia may be expelled, and the residual sulphate of zinc will be quite pure; but if the salt be suddenly heated, a quantity of sulphate of ammonia is produced, and the sulphate of zinc remaining is mixed with oxide.

As this salt, from the manner of its formation, must contain two equivalents of ammonia to one of the sulphate of zinc, the analysis of it became very simple, as it was to be directed specially to the examination of the quantity of water which it might contain.

In efflorescing this salt does not lose ammonia. To determine its composition, 3.701 of clear crystals, dried between folds of blotting-paper, were heated at first very gently, but finally to ignition. On the first application of the heat the salt fused, and emitting water and ammonia, left a perfectly white residue of sulphate of zinc, weighing 2.023, corresponding to 54.66 per cent. Its composition, therefore, is:

$$\begin{aligned} \text{Sulphate of zinc} &= 54.66 \\ \text{Volatile matter} &= 45.34 \end{aligned}$$

and

$$\frac{54.66}{45.34} = \frac{80.50 = ZnO.SO_3}{66.77 = 34.28\,NH_3 + 32.49}$$

Consequently the water is $\frac{32.49}{9} = 3.61$ equivalents, and as the salt is efflorescent, the true number is probably four.

When these crystals have been left in the open air for some time they lose altogether their transparency, but retain their form, assuming the milky lustre of the crystals of nitrate of lead. When these milky crystals are heated they melt, and are decomposed with precisely the same phenomena as the transparent ones, leaving a sulphate of zinc redissolving completely in water.

3.030 of these crystals, so treated, gave 1.818 of sulphate of zinc, or 60 per cent.; hence,

$$\text{as } \frac{60}{40} = \frac{80.5}{53.66} \text{ and } 53.66 - 34.28 = 19.38.$$

The quantity of water had evidently been reduced to one-half by efflorescence, no ammonia having been lost, as was ascertained by experiment.

In the decomposition of this salt by heat, the ammonia and water go off together to the end, and this is easily seen, as the material lost is exactly $2(NH_3.HO)$.

By the first application of the heat it was mentioned that the salt fused after it had lost a certain proportion of gas and water; this fused mass, on cooling, solidifies into a mass like gum, which may be again melted, and the remaining ammonia and water expelled, as above described. In order to ascertain whether the fusion of the mass occurred at any definite point in the process of decomposition, a quantity of the effloresced salt was heated until completely fused, the lamp was then removed, and the weight of the residual gummy-looking material determined,—it amounted to 80.29 per cent.; and hence it results that the quantity of volatile matter lost had been exactly half of the entire amount, thus,

$$\left.\begin{array}{llcr} & \text{Sulphate of zinc} & = & 60.00 \\ a. & \text{Volatile matter} & = & 20.29 \end{array}\right\} \text{Gummy residue.}$$

$$\begin{array}{llcr} b. & \text{Volatile matter} & = & 19.71 \\ \hline & \text{Effloresced salt} & = & 100.00 \end{array}$$

From these results follow the formulæ

Transparent crystals = $ZnO.SO_3+2NH_3+4HO$
Effloresced crystals = $ZnO.SO_3+2NH_3+2HO$
Gummy mass = $ZnO.SO_3+NH_3+HO$
Which gives by heat = $ZnO.SO_3$

I shall, before proceeding further, return to the examination of the flocculent substance which was deposited from the hot solution of the ammonia-sulphate. It cannot be redissolved in water, which distinguishes it from the transparent crystalline salt; when heated it fuses, and is decomposed with the escape of water and ammonia, as is the case with the substance already described. It was analyzed as follows:

5.033 of this flaky substance was heated until all escape of water or of ammonia had ceased; there remained 3.821 of sulphate of zinc, corresponding to 75.92 per cent., and

$$\frac{75.92}{24.08}=\frac{80.50}{25.53}, \text{ and } 25.53-17.14=8.39, \text{ or nearly } 9.$$

Hence the formula is $ZnO.SO_3+NH_3+HO$.

These flakes have therefore the same composition as the gummy mass obtained by melting the crystalline salt, and this circumstance proves that the gummy mass is really a definite chemical compound, which could not have been so positively shown from the method by which it had been prepared.

When the crystalline salt is kept for some time at a temperature of from 80° to 100° F. it gradually falls down into a white powder, all traces of crystalline structure having totally disappeared; during this decomposition, water alone escapes, as turmeric paper left on the surface of the powder is not at any period affected. When this powder is heated to about 212°, it gives out water and ammonia, which continues up to a certain point, but in order to finish the expulsion of the water, the temperature must be raised until the mass has become fused;

after that time, the continuance of the heat occasions the loss of more ammonia, but no more water is disengaged. Unless the heat be very accurately managed, sulphite of ammonia is apt to make its appearance before the last portions of the ammonia have been expelled; with care, however, a sulphate of zinc almost completely soluble in water may be obtained.

To determine more closely what occurs in the case just noticed, 4.238 grammes of the powder formed by the efflorescence, at 100°, of the crystals were heated until the sulphate of zinc remained pure behind; it weighed 2.800, or 66.07 per cent.

4.385 of the same powder were heated until it had fused, and the escape of water had ceased, great care being taken to seize the precise time, and to avoid the application of any unnecessary heat; the residual mass weighed 3.470, or 79.13 per cent.

$$\text{Now } \frac{66.07}{33.93} = \frac{80.50}{41.34}, \text{ and } 41.34 = 32.34 + 9, \text{ q. p. } 2\,\mathrm{NH_3} + \mathrm{HO}.$$

The proportion of ammonia being a little less than two atoms.

Again, the second experiment gives

$$\left.\begin{array}{ll} zn\mathrm{O.SO_3} & 66.07 \\ \text{Ammonia} & 13.06 \end{array}\right\} = 79.13 \text{ of residual fused mass;}$$

and

$$\frac{66.07}{13.06} = \frac{80.50}{15.91}, \text{ or nearly } \frac{80.50}{17.14} = \frac{zn\mathrm{O\,SO_3}}{\mathrm{NH_3}}.$$

The effloresced powder was therefore

$$zn\mathrm{O\,SO_3} + 2\mathrm{NH_3} + \mathrm{HO},$$

corresponding to the crystallized ammonia-sulphate of copper, and by heat it loses $\mathrm{NH_3}\,.\,\mathrm{HO}$, and there is formed

$$\mathrm{SO_3}\,.\,zn\mathrm{O\,NH_3},$$

being precisely the same as in the copper series. This effloresced powder put into water dissolves almost without residue, provided the water be free from carbonic acid.

The reasoning which I employed concerning the rational formulæ of the ammoniacal compounds of copper, applying with equal force to those of zinc, I will not repeat it, but arrange the results just now described, in accordance with those views.

1. The crystalline salt $= (NH_3 . HO)\, SO_3 + ZnO . (NH_3 . HO) + 2\, HO$.
2. The effloresced crystals $= (NH_3 . HO)\, SO_3 + ZnO\, (NH_3 . HO)$.
3. The effloresced powder $= (NH_3 . HO)\, SO_3 + ZnO . NH_3$.
4. The flakey substance $= (NH_3 . ZnO) . SO_3 + HO$.
5. The fused mass from 3 $= (NH_3 . ZnO) . SO$.

I will not enter into the consideration of any of the interesting relations which the arrangement of this series of bodies must suggest, except to point out in the ordinary sulphate of ammonia, the anomaly of the crystallization of which, with an atom of water, is so curious, the analogue of the bodies 4 and 5. Thus there is

$$(NH_3 HO.)\, SO_3 + HO \text{ and } (NH_3 . HO)\, SO_3$$

as there is

$$(NH_3 . ZnO)\, SO_3 + HO \text{ and } (NH_3\, ZnO)\, SO_3.$$

When discussing the theory of these bodies in another section, I shall have occasion to recur to these results.

XI. OF A NEW BASIC SULPHATE OF ZINC.

When the bodies (4) or (5) are treated by water they are decomposed, the body (1) dissolves, a quantity of sulphate of ammonia is likewise formed, and the insoluble matter is so definite and marked in its composition, that it must be regarded as a new basic sulphate of zinc. It is white, insoluble in water, when heated it gives water, and leaves a white powder behind. It was analyzed as follows:

2.594 grammes, dried by a spirit-lamp, gave 1.950, or 75.18 per cent., having lost 24.82 water.

The residual sub-sulphate was boiled with solution of carbonate of soda, and the carbonate of zinc collected on a filter, dried, and ignited; the oxide of zinc remaining weighed 1.635, or 64.22 per cent. Hence the composition

Sulphuric acid	=	10.96
Oxide of zinc	=	64.22
Water	=	24.82

2.544, dried, gave 1.957, from whence

Dry sub-sulphate	=	75.88
Water	=	24.12

The dry mass, exposed to the air, absorbed water, and became 2.137, or 8.40 per cent., having taken up almost exactly one-third of the quantity of water it had lost.

These results point out the formula

$$SO_3 + 6ZnO + 10\,HO,$$

which should give

SO_3	=	40.16	10.79
$6ZnO$	=	241.80	65.02
$10HO$	=	90.00	24.19
		371.96	100.00

There are two sub-sulphates of zinc already known, of which the one $SO_3 + 4ZnO$ has been described by Schindler, Kuhn, and Graham. It appears to combine with variable proportions of water, from two to ten equivalents, but most commonly is to be found with four. The second has been examined by Schindler alone, who gave its formula as $SO_3 + 8ZnO + 2HO$. I have not had an opportunity of verifying this result, but I consider the correctness of his analysis as being very probable. The same chemist showed that there may be formed a soluble compound of $SO_3 + 2ZnO$, which, however, is destroyed when dried. Hence the series of basic sulphates of zinc may be thus arranged:

Real neutral sulphate = $ZnO \,.\, SO_3$.
Salt with saline water = $(ZnO.HO)\,SO_3$.
Soluble salt of Schindler = $(ZnO \,.\, ZnO)\,SO_3$.
Common crystals = $(ZnO \,.\, HO)\,SO_3 + 6HO$.
Hyperbasic salt, dry = $(ZnO \,.\, ZnO)\,SO_3 + 6ZnO$.
Common basic salt, dry = $(ZnO \,.\, ZnO)\,SO_3 + 2ZnO$.
Do. with water—Schindler = $(ZnO \,.\, ZnO)\,.\,SO_3 + 2ZnO + 2HO$.
New basic salt, dry = $(ZnO \,.\, ZnO)\,SO_3 + 4ZnO$.
Do. with water = $(ZnO \,.\, ZnO)\,SO_3 + 4ZnO + 10HO$.

The law of replacement being precisely what was already shown in the copper series, but still more complete from the discovery of $SO_3 + 6ZnO$.

PART III.

ON THE THEORY OF THE AMMONIACAL COMBINATIONS.

ON the accession to science of any considerable body of new facts, we should carefully examine how far they tend to modify our ideas of the nature and intimate structure of the bodies to which they relate, and of the forces to the action of which these bodies are subjected, and by remodelling our views in accordance with the ideas thus obtained, we should endeavour after a closer approximation to that truth, the attainment of which is the object of all scientific labour.

A body, possessing so many interesting properties as ammonia, standing as it were, on the confines of mineral and of organic chemistry, and forming the connecting link between them, must even, on its own account, and still more from the remarkable variety of classes of combinations into which it enters, occupy a prominent place in the general theory of chemistry, and the grounds of any proposed alteration in our views concerning it should be examined with the attention due to the importance of the subject. I shall therefore lay before chemists, for discussion, some views of its nature and laws of combination, differing in many important particulars from those hitherto received, which have been suggested to me by the researches on the various classes of compounds of ammonia contained in the present and former papers. These views are connected in a very remarkable manner with those concerning which the opinions of chemists have been so long divided; it will be seen, in fact, that the principles of the theory which I propose, embrace all that was vital in former hypotheses; and it may be almost considered as an argument for its sufficiency, if not actual truth, that in the development of these views is exemplified the ordinary course of advancing knowledge, when the once conflicting elements of rival theories are found forced into coalition by the grasp of some generalization of a higher order.

Before commencing the explanation of my own views, I shall briefly describe the essential principles of the previous theories of ammonia.

A.—The oldest view:

1. That ammonia NH_3 is an independant base, saturating acids and forming salts.

If, as Dulong proposed, all acids be regarded as hydrogen compounds, thus $SO_3 + HO$ as $SO_4 + H$, similar to ClH, the old view explains the main requisite in all theories of ammonia, the presence of water in the salts formed by the oxygen acids. Sulphate of ammonia becomes $SO_4.H + NH_3$, like $Cl.H + NH_3$.

B.—The theory of Berzelius:

1. That the ammoniacal amalgam contains a body, NH_4, which is metallic, combines with oxygen, and then may replace potash in combination.
2. That when NH_3 combines with HCl. the NH_3 takes H, and forms NH_4, with which the chlorine combines.
3. That the water in the ammoniacal salts with the oxyacids converts NH_3 into $NH_4 + O$.

C.—The amide theory, as left by Dumas and Berzelius:

1. There was assumed a hypothetic body, NH_2, which replaced chlorine and oxygen in certain organic combinations.
2. Potassium or sodium heated in ammonia, liberated therefrom as much hydrogen as from water, and formed amidide of potassium or of sodium.

Ammonia is in no place called amidide of hydrogen by Berzelius or by Dumas, nor is NH_3 ever written $NH_2 + H$, but Dumas may have had that idea indistinctly in his mind when he said that it was perhaps possible that as hydrogen forms hydracids with some bodies, so it might produce hydrobases by its union with others. He may have meant that hydrogen formed ammonia, a hydrobase, by uniting with NH_2 amidogene, but he much more probably referred to the combination of the hydrogen at once with nitrogen; his adherence to the common, but incorrect ideas of the nature of the hydrogen bodies in general having completely prevented him from seeing the true position of ammonia and its compounds.

The insufficiency of these views may be very briefly pointed out; thus,

A.—The oldest view.

1. It applies only to the common ammoniacal salts, but does not attempt any explanation of the nature of the numerous other classes of ammonia compounds.

2. It states merely that NH_3 acts as a base, but does not explain its relation to ordinary bases which are metallic oxides, nor the points in which the ammoniacal salts differ from the metallic salts of the same acid.

B.—The Berzelian view.

1. It does not assign any proper function or place to ammonia itself, which might be absolutely dropped out of the theory without loss. This view, therefore, leaves unexplained all combinations of ammonia with bodies which do not contain hydrogen.

2. That $NH_3 + H.Cl$ becomes $NH_4 + Cl$, is purely hypothetical, and highly improbable, the ammonia not exercising any apparent affinity for hydrogen, while that of chlorine for hydrogen is very strong. Hence the duty of proving the change in position of the fourth atom of hydrogen rests with the Berzelian theory, and has not been yet performed.

C.—The amide theory.

1. Our knowledge of the amidogene combinations has been acquired almost exclusively since the theories just noticed had been proposed, and consequently what is now the most important principle in a complete theory, the connexion of the ammonium and of the amidogene compounds with those containing ammonia itself had no place therein. Hence all former theories are insufficient, from the ground that the new facts gained by the study of the metallic amidides cannot be explained by or included within the principles upon which they rest.

I shall now describe, in a series of propositions, the principles of the theory which I advocate, and then taking each proposition by itself, will sum up the evidence derived from experimental results, by which I consider its validity to be established.

PROP. I.—That the so called hydracids are not really such; that hydrogen, in all its forms of combination, is analogous to certain metals of the electropositive class, and its compounds react like theirs under similar circumstances.

II.—That ammonia NH_3 is amidide of hydrogen $NH_2 + H$, and resembles in some respects the oxide, in others the chloride of the same positive element.

III.—That NH_2 amidogene may combine with metals, and that the metallic amidides have a singular tendency to combine with the chlorides or oxides of the same metal, or of a metal of the same family, and thus form bodies resembling the chloro-oxides, chloro-sulphurets, or oxysulphurets.

IV.—That $NH_3 = NH_2 + H$ amidide of hydrogen can perform the same functions in combination as water, oxide of hydrogen, whether as basic water, or water of crystallization, and likewise can replace the water termed saline in certain salts by Graham.

V.—That the so called oxide of ammonium NH_4O is oxy-amidide of hydrogen $NH_2 . H + HO$, and that sal ammoniac is chloro-amidide of hydrogen $NH_2 . H + HCl$.

VI.—That the ordinary ammonia salts ally themselves to the salts of the copper and zinc class, which contain two equivalents of oxide.

VII.—That if chlorine could be separated from sal ammoniac, the residual NH_4 should be regarded as $NH_2 + 2H$, sub-amidide of hydrogen, as when by removing the chlorine from white precipitate, the sub-amidide of mercury, $NH_2 + 2Hg$, formed by the action of water of ammonia on calomel, should remain.

Prop. I.—*Of the general positive Nature of the Compounds of Hydrogen.*

In a memoir which was published in 1831 in the Dublin Journal of Medical and Chemical Science, I pointed out that the general bearing of the properties of the compounds of hydrogen should induce us to assign to those bodies a totally different position from that which the names of hydrogen-acids previously assigned to most of them would appear to warrant. Thus that, whilst we found hydrogen to manifest immensely superior electro-positive energies to those of gold, platinum, or sulphur, it was quite unphilosophical to suppose, that when all of these bodies were combined with chlorine, the hydrogen should be that least capable of diminishing the negative power of the chlorine. I showed that from the considerations which are suggested to us by a fair comparison of the properties of the oxides, chlorides, sulphurets, &c. of hydrogen, with those of the similar compounds of the metals, it became quite necessary to allow, that although in some cases, as where water united with potash or lime, the hydrogen body may perform the negative function, yet in the vast majority of cases the part played by it in combination is that of positive constituent.

I shall refer to the memoir above quoted for the details of the views which I then brought forward; previously to that time Mitscherlich had already suggested, that in the hydrated acids the water acted as a base, but this, from the indifferentism of water in the generality of chemical actions, could not be considered as leading to any thing like the general principle which formed the subject of my paper. Since that period, although no writer has broadly reproduced this theory of the hydrogen combinations, yet the progress of research has gradually lent to it the most efficient support, by the discovery of classes of bodies identifying in the strictest manner the chemical relations of hydrogen, and of certain of the more positive among the metals. The beautiful investigations of Graham on water as a constituent of salts, particularly those illustrating the conversion of the neutral into the basic condition by the replacement of the hydrogen by a metal of the magnesian family, has shown that in its relations to oxygen at least no line of distinction can be drawn between hydrogen and the metals which with it constitutes so natural a group.

Passing to the other compounds of hydrogen, there will be found in the series of researches on the zinc and copper families, a variety of instances in which the chloride of hydrogen is represented with remarkable closeness by the chlorides of copper or of zinc. The examination of the various oxychlorides of zinc, in their dry and hydrated conditions, which presents to us the perfect analogues of the chloride of hydrogen in its two stable conditions of definite combination with water, points out an identity of action liable to little objection. Like the chloride of hydrogen also, chloride of zinc is caustic, and when concentrated reddens litmus, so that the peculiarly acid character of affecting that reagent is to be found well developed in bodies to which, under any circumstances of ordinary language, the name of acid could scarcely be applied.

The relation of chloride of zinc to ammoniacal gas is likewise very remarkable, as indicating the general similarity of action between the hydrogen and zinc compounds: the volatility of the ammonia-chloride of zinc, the permanent nature of the ammonia-chloride of copper, indicate a closeness of union between the metallic chloride and the ammoniacal gas, which brings those bodies into very intimate connexion indeed with sal ammoniac.

As this proposition will receive from the evidence of several of the succeeding ones a great deal of additional support, I will not here enter into any further evidence in favour of it. Every fact which, in the course of these researches, became the subject of examination, has tended to strengthen my confidence in the truth of the general principle which the additions to science from the recent investigations of other chemists have likewise uniformly tended to confirm.

Prop. II.—*That ammonia* NH_3 *is amidide of hydrogen, and should be written* $NH_2 + H$.

The re-examination of the results of Gay Lussac, Thenard, and Davy, on the action of potassium on ammoniacal gas, gave to the interesting views of Dumas, arising from the discovery of oxamide, a stability and importance which must be considered as the origin of all subsequent investigations in that extensive field. When we allow for the various sources of error to which, from the easy decomposition of the resulting bodies, the quantitative determinations of the hydrogen evolved from the ammonia is exposed, we shall find in the experiments of those exact chemists a complete proof that potassium liberates from ammonia precisely the same quantity of hydrogen as from water, and hence that the element remaining united with the potassium is amidogene. The idea of ammonia being itself a base differing essentially in constitution from the oxides of hydrogen or of the metals, prevented the distinguished discoverer of oxamide from tracing in the action of potassium on ammonia, the rational constitution of the latter, and although he recognized completely the identity of function performed by the metal in the one case, and the carbonic oxide in the other, yet it is evident, from the tenor of his observations on all occasions, that he looked upon the abstraction of the equivalent of hydrogen as subverting the constitution of the ammonia, and that the amidogene resulting did not stand in any natural relation to the ammoniacal gas employed.

Notwithstanding the remarkable cases discovered and examined by Henry Rose, in which the combinations of ammonia with the various classes of salts appeared to correspond so closely with the same salts containing water of crystallization, whence, taken in connexion with the existence of the amidides of potassium and sodium, the symmetricity of NH_3 and OH might be inferred, and the form $NH_2.H$ given to the former; yet, until the discovery of the composition of white precipitate, and of the similar bodies which I examined, and which was fundamental to all these researches, instances of the resolution of ammonia into amidogene and hydrogen, independent of all destructive action, had not become sufficiently positive and unexceptionable to lead any chemist to express the opinion of its being really amidide of hydrogen, ranking with the oxide and chloride of the same element. This view, however, results almost unavoidably from those experiments, although I myself did not finally adopt it until by the development of the nature of the other quicksilver combinations with ammonia, the complete identification of the principle of action of oxygen and amidogene, particularly as exerted in the two classes of water and of ammonia sub-salts, left no room in my mind for any other hypothesis.

The objection to the assumption of the existence of an hypothetic body, amidogene, which might be supposed to weigh powerfully against the general acceptance of this theory, is deprived of a great deal of its force when we come to examine it with somewhat more care. In order to arrive at an idea of the actual nature of ammonia, and of the position it is suited to occupy in the general scheme of chemical reactions, we must investigate the laws of its affinities, and study accurately the analogies which it presents in its combinations, with those of other bodies of simpler constitution, and the history of which is as yet better understood. From these data must our conclusions be drawn, and decompositions, frequently of an accidental character, and mostly dependant on the peculiar manner in which the affinities of the decomposing body may be exerted, should be considered of but secondary importance, and subordinate to the study of the general history of the substance, although still suited, under proper limitations, to guide us usefully in our course. It is right that the exertions of chemists should be directed to effect the isolation of amidogene, and it is to be hoped that the same success which crowned the beautiful researches of Gay Lussac on Prussic acid, will reward their efforts; but even should this radical, like those of so many of the most important series in organic chemistry, for a longer time elude our grasp, it is proper and just to assume it to exist, if we, by so doing, can obtain a more satisfactory explanation of phenomena, and link together classes of facts previously disconnected and obscure.

Prop. III.—*That amidogene may combine with metals, and that the metallic amidides have a singular tendency to combine with the chlorides or oxides of the same metals.*

The formation of the amidides of potassium and sodium, gives sufficient proof of the first part of this proposition, and there have been found in the researches on the ammoniacal combinations of quicksilver, numerous instances of the truth of the latter principle. Thus white precipitate must be looked upon as a compound of chloride and amidide of mercury, and the black substance formed by the action of water of ammonia on calomel must be composed of sub-chloride, united to the sub-amiduret of the same metal. More complex examples are furnished by the yellow powder

$$\mathrm{Hg}\,cl + 2\,\mathrm{Hg}\,\mathrm{O} + \mathrm{Hg}\,.\,\mathrm{NH}_2,$$

and the bodies

$$\mathrm{Hg}\,\mathrm{SO}_4 + 2\,\mathrm{Hg}\,\mathrm{O} + \mathrm{Hg}\,\mathrm{NH}_2$$
$$\mathrm{Hg}\,\mathrm{NO}_6 + 2\,\mathrm{Hg}\,\mathrm{O} + \mathrm{Hg}\,\mathrm{NH}_2.$$

In the copper family there exist some examples equally remarkable, but which shall be referred to particularly under a distinct head.

Prop. IV.—*That amidide of hydrogen can perform the same functions in combination as oxide of hydrogen, whether as basic water, as water of crystallization, or as the water termed saline by Graham.*

In the most perfect cases of substitution, where the substances belong to strictly isomorphous groups, the similarity of properties and structure existing through the several classes of bodies formed by the mutually replacing elements, assumes an exactness to which no parallel is found in the instances with which the history of the ammoniacal bodies has supplied us; yet amongst the combinations described in the preceding sections, analogies and relations have been observed of such closeness, as to give to the truth of the proposition now in question the highest probability.

A vast number of bodies, such as oxygen-salts, chlorides, iodides, &c., exposed to the action of ammoniacal gas, absorb a considerable quantity thereof, and it is afterwards found that different portions of this ammonia are retained with various degrees of force: the greater part being, generally speaking, expellable by the temperature of boiling water, whilst the remainder clings to the substance with a much higher power, sometimes not being separable, unless the constitution of the body be completely broken up. This fact finds a complete parallel in the relative degree of affinity with which water is retained by ordinary salts and acids. Thus the retention of the basic water by oxalic and common tartaric acids, and the greater affinity of the last atom of water in the sulphates of the magnesian class find in the compounds of ammonia their analogous combinations, and one of the most embarrassing circumstances in the present investigation arises from the fact of the relation of ammonia and water being so close, that where the ammoniacal bodies are soluble in water, they cannot be brought into contact with it without an exchange of position occurring to a considerable extent, and the body crystallizing in a state containing both water and ammonia. Thus, whilst by passing dry ammonia over chloride of copper, the body $cucl + 3NH_3$ may be obtained, the result of treating a solution of chloride of copper by ammonia is $cucl + 2NH_3 + HO$, in which the third equivalent of ammonia has evidently given place to one of water; and though the copper, as I have already shown, is separated from the chlorine, however by means of heat both bodies yield $cuclNH_3$; the one losing $2NH_3$, the other $HO.NH_3$. Thus, through the whole class of soluble ammonia-copper and zinc combinations, the water replaces, in the first instance, the metallic constituent, and partly the ammonia itself, and it is only when by the application of heat the water with some ammonia has been expelled, that we arrive at the real combinations of the metallic compound with amidide of hydrogen.

The basic nitrates of mercury being insoluble, furnish one of the most striking examples to be found of the replacement of water in its basic condition by ammonia. It was proved that the basic nitrates stood in the same relation to the neutral salts as that which Graham had pointed out for the nitrates of the magnesian class; and I showed, in the same section, that the ammonia subnitrates were so constituted, that the nitric acid and oxide of mercury remained the same, whilst the water of the ordinary sub-salts was replaced by the ammonia thus: Ad representing NH_2. amidogene.

The yellow sub-nitrate of the red oxide is

$$HO.NO_5 + 3Hgo.$$

The ammonia sub-nitrate of the red oxide is

$$HAd.NO_5 + 3Hgo.$$

The sub-nitrate of the black oxide is

$$HO.NO_5 + 2\underline{Hg}o.$$

The ammonia sub-nitrate of the black oxide is

$$HAd.NO_5 + 2\underline{Hg}o.$$

These examples establish, in this case, the complete similarity of action of hydrogen, whether combined with oxygen or amidogene.

In the second part of the present memoir will be found a remarkable instance of the replacement of water by ammonia. There was described a new chloroxide of copper, $cucl + 2cuo$; this unites with water, forming a brown powder,

$$cucl + 2cuo + \mathrm{HO},$$

evidently analogous to dry Brunswick green,

$$cucl + 2cuo + cuo\,;$$

but it also unites with dry ammonia to form a brown powder,

$$cucl + 2cuo + \mathrm{HA}d\,;$$

under which form the replacement of HO by cuo, and of both by $\mathrm{HA}d$, is evidently shown.

When once the principle of ammonia being considered as amidide of hydrogen, has been steadily brought before the mind, the nature of a vast class of combinations, the functions of the ammonia in which had previously presented great difficulty, is at once cleared up. Thus the combinations of ammonia with the chlorides of tin, of antimony, of phosphorus, &c. are at once seen to resemble those which many of the same bodies enter into with water, in equally definite proportions; thus $sncl_2 + \mathrm{HA}d$ is a white solid body, and $sncl_2 + \mathrm{HO}$ is equally white and solid. The compounds of the chlorides and oxysalts of the magnesian class of metals present a parallelism still more close, and to which, after some time, I shall again refer.

A class of bodies, the nature of which has frequently given occasion to discussion, is the combinations of the oxygen acids with dry ammonia. Of these, the most remarkable and the most accurately studied is that with sulphuric acid, and I shall consider it in these observations as the type of the whole class.

There are two opinions of the nature of this body,—first, that which vaguely considering ammonia as a base *per se*, looks upon the existence of two classes of ammoniacal salts, one merely of ammonia, the other of oxide of ammonium, as possible, and enumerates this and other similar bodies in the former group; second, that which considers the sulphuric acid and ammonia as being mutually decomposed, and water being formed, an amidide to be produced, with which the water remains united. Thus there is $SO_3 + NH_3$ or $SO_2.NH_2 + OH$.

From the latter view, although supported by the high sanction of Dumas and many others, I must dissent. We have no reason to suppose water to be contained in the compound in this eliminated form; and unless we find no other legitimate method of explaining its origin and properties, an hypothesis of that kind should not be resorted to.

Previous to discussing the first point of view, I must make some observations as to the view of ammonia being an independent base. This phrase has had its origin in the earliest age of organic chemistry, when the volatile ranking with the fixed alcalies, chemists were contented with the observation that there were salts of ammonia, as there were salts of potash and soda, without recognizing accurately any difference of type of constitution amongst them. The progress of analysis, however, pointed out the presence of water in all ordinary ammoniacal salts of the oxygen acids, and hence the notion of the independent basic power of ammonia became almost forgotten. Indeed, if one examines what is said by systematic writers on the combinations of the dry acids with dry ammonia, it will be found that no definite or distinct idea of their nature has been formed; that they are grouped together to separate them from the real ammoniacal salts, which are said to contain ammonium, but that no opinion of their intimate constitution has been hazarded even by Berzelius. In fact in order to understand their nature, our opinions as to the words *acid* and *base* must be reviewed. We can no longer look upon oxygen as being the sole negative element of basic bodies, since sulphur identifies itself with it in all its principles of action, and the analogy has been extended with some justice even to chlorine, iodine, and bromine. Hence there can be no doubt but that amidogene, which relates itself to oxygen so closely in a multiplicity of instances, may form the negative element in combinations of this kind, and as water, oxide of hydrogen, acts as a base, so may ammonia as amidide of hydrogen. The difference between the vague old idea of ammonia as an alkali, and the definite principle of the basic power of amidide of hydrogen will be at once felt; in fact the alkali, the body which resembles and replaces in combination the other alkalies, potash and soda, is not ammonia, but ammonia and water, not amidide of hydrogen, but oxide of ammonium, (of Berzelius). Whilst the amidide of hydrogen, ammonia alone, is analogous to, and replaces oxide of hydrogen, or the oxides of the magnesian class of metals. It is this distinctness in the point of view which will enable us to apply this principle in a useful manner.

Now, taking the instance before described, there is

$$\mathrm{H.O} + \mathrm{SO}_3, \text{ similar to } \mathrm{H.A}d + \mathrm{SO}_3;$$

and the circumstance of the latter not precipitating barytes water, or chloride of barium, is at once seen to result from the heterogeniety of the negative ingredients in the two cases; because, arranging the formulæ according to Dulong's view, to which the opinions of chemists now so generally incline, there is

$$\mathrm{H} + \mathrm{SO}_4 \text{ and } \mathrm{H} + \mathrm{A}d\mathrm{SO}_3;$$

and the formation of $\mathrm{B}a.\mathrm{SO}_4$, which results naturally in the former case, becomes complicated and difficult in the latter. In fact the body $\mathrm{A}d\mathrm{SO}_3$ is quite distinct from any thing belonging to sulphuric acid, and can only give origin to it from a complete destruction of the powerful affinities by which it was at first produced.

This view of the basic action of ammonia, and of its relation to acids, will be found to lead to considerations of the highest interest to organic chemistry, but which it would be improper to introduce here, in the detail which alone could be of use.

PROP. V.—*That the so called oxide of ammonium,* $\mathrm{NH_4O}$, *is oxyamidide of hydrogen, and that sal ammoniac is chlor-amidide of hydrogen.*

The only reason which has been advanced in support of the Berzelian ammonium theory, is the beautiful symmetry with which the ammoniacal and potash salts are by it invested, and that as the similarity and replacing power of $\mathrm{OH.NH_3}$ and OK constituted one of the best authenticated facts in the doctrine of isomorphism, it was but reasonable to suppose the corresponding portions of those symbols, $\mathrm{HNH_3}$ and K to belong to the same class. The circumstance also of the ammoniacal amalgam preserving so perfectly a metallic appearance, although its density becomes so wonderfully diminished, lent to the idea of the existence of a metal (ammonium) powerful support; and there is indeed nothing in the theory which I now bring forward to negative the leading principles of that view, by the adoption of which so great simplicity had been conferred on the history of the ammonia salts. Thus according to my ideas, as well as in the Berzelian view, the $cl\mathrm{NH}_4$ replaces $cl\mathrm{K}$, and ONH_4 replaces OK in combination, and also NH_4, if isolated, should be considered as fulfilling the functions of K; but in the theory now proposed an additional step is made, by which we are conducted to a closer and more distinct view of the inner constitution of these bodies.

When we place in contact two substances both compound, and which mutually combine, in order to judge of the mode in which these elements unite, we must examine the nature of the affinities by which a breaking up of the original constitution might be effected, and likewise those which would tend to maintain the two constituents in their primitive condition, and allow merely of their union with one another. On these circumstances, and by the general mode of reaction of the new substances formed, must the construction of its rational formula be founded. If we contemplate the reaction of dry chloride of hydrogen and amidide of hydrogen, when brought into contact, we shall not be able to trace any tendency in the latter to deprive the chlorine of the hydrogen with which it is united; on the contrary, we find the affinity of chlorine for hydrogen so preponderating, that ammonia, by its agency, may be reduced to simple azote. It is therefore contrary to all first principles of chemical affinity to believe, that in the combination of the chloride with the amidide of hydrogen, all the hydrogen can exist in one group of the formula, whilst chlorine alone constitutes the other; since, if we had amidogene or ammonium isolated, there can be no doubt but that chlorine could take hydrogen from both. That assumption could only become justifiable if rendered necessary by strongly corroborating facts, and it will be found that no facts at all sufficiently in point can be brought forward.

Regarding ammonia as amidide of hydrogen, its union with chloride of hydrogen becomes but a particular case, although one of the most important, of the general tendency of chlorides, oxides, and amidides of the same or of similar radicals, to unite and form double chlor-oxides, chlor-amidides, or oxamidides. In fact, if we look to the formation of white precipitate by corrosive sublimate and water of ammonia, it will be seen that the decomposition and combinations are on each side quite symmetrical; thus, there is

$$2\mathrm{H}g\,cl + 2\mathrm{HA}d = (\mathrm{H}g\,cl + \mathrm{H}g\mathrm{A}d) + (\mathrm{H}cl + \mathrm{HA}d).$$

The two resulting compounds, white precipitate and sal ammoniac, being strictly bodies of the same type, one containing quicksilver and the other hydrogen.

I sought very frequently to obtain sal ammoniac combined with water of crystallization, in order to produce a parallel to the compound

$$\mathrm{H}g\mathrm{C}l + 2\,\mathrm{H}g\mathrm{O} + \mathrm{H}g\mathrm{A}d,$$

but unsuccessfully. Yet if we consider the close relations of hydrogen and copper, and of oxygen and amidogene, we will find in the bodies

$$\begin{gathered}\mathrm{C}u\mathrm{C}l + 2\,\mathrm{C}u\mathrm{O} + \mathrm{HO}\\ \mathrm{C}u\mathrm{C}l + 2\,\mathrm{C}u\mathrm{O} + \mathrm{C}u\mathrm{O}\\ \mathrm{C}u\mathrm{C}l + 2\,\mathrm{C}u\mathrm{O} + \mathrm{HA}d\end{gathered}$$

similar cases, in the same way as quicksilver, gives

$$\mathrm{H}g\mathrm{C}l + 2\,\mathrm{H}g\mathrm{O} + \mathrm{H}g\mathrm{O}\,;$$

and also the soluble ammonia chloride of copper, whether written

$$\mathrm{C}u\mathrm{C}l + 2\,\mathrm{HA}d + \mathrm{HO},$$

or

$$(\mathrm{HC}l + \mathrm{HA}d) + (\mathrm{C}u\mathrm{O}.\mathrm{HA}d),$$

presents analogies fully supplying the place of hydrated sal ammoniac.

To sal ammoniac itself the copper and zinc series affords numerous analogues. Thus, the perfectly definite and well characterized bodies,

$$\begin{gathered}1.\ \mathrm{C}u\mathrm{C}l + \mathrm{HA}d.\\ 2.\ \mathrm{Z}n\mathrm{C}l + \mathrm{HA}d.\\ 3.\ \mathrm{N}i\mathrm{C}l + \mathrm{HA}d.\end{gathered}$$

correspond to

$$\mathrm{H}.\mathrm{C}l + \mathrm{HA}d\,;$$

whilst we find for the ordinary compound

$$\mathrm{C}u\mathrm{C}l + (\mathrm{H}.\mathrm{C}l + \mathrm{HA}d) + 2\,\mathrm{HO},$$

the body

$$\mathrm{Z}n\mathrm{C}l + (\mathrm{Z}n\mathrm{C}l + \mathrm{HA}d)$$

and also

$$\mathrm{Z}n\mathrm{C}l + (\mathrm{Z}n\mathrm{C}l + \mathrm{HA}d) + (\mathrm{HO}.\mathrm{HA}d),$$

or else

$$\mathrm{Z}n\mathrm{C}l + (\mathrm{HC}l + \mathrm{HA}d) + (\mathrm{Z}n\mathrm{O}.\mathrm{HA}d).$$

These analogies are so remarkable, that any detailed comment on them is unnecessary.

Since the oxide of ammonium of Berzelius possesses a definite constitution only in the salts of oxygen acids with which it may unite, the superior simplicity and distinctness of the present view becomes still more remarkable in its case than in the former. We have seen that in combination with oxides the amidide of hydrogen or of the metals assumes, even in the simplest cases, very complicated formulæ; thus, the

Oxamidide of mercury is

$$\mathrm{H}g\mathrm{A}d + 2\mathrm{H}g\mathrm{O} + 3\mathrm{HO}.$$

Oxamidide of copper is

$$2\mathrm{C}u\mathrm{A}d + \mathrm{C}u\mathrm{O} + 6\mathrm{HO}.$$

Oxamidide of gold is

$$2\mathrm{A}u\mathrm{A}d_3 + \mathrm{A}u\mathrm{O}_3 + 6\mathrm{HO}.$$

When, therefore, we come to examine the constitution of water of ammonia, a similarly large number of molecules may be expected to be contained in its equivalent group, and in the fact of all the oxamidides above described, and also that of silver, the analysis of which I was obliged to abandon, being the most dangerous and explosive bodies, we may trace the source of a facility of decomposition in the oxamidides of hydrogen, which prevents us from obtaining even the degree of definite constitution which has been found to exist in the hydrates of the chloride of hydrogen, although the approximation in the strongest water of ammonia to the formula $\mathrm{NH}_3 + 4\mathrm{HO}$ cannot be overlooked; and therein also we find the explanation of the want of success in obtaining, in an isolated form, the oxide of ammonium, which has always been, and must continue, an objection to the Berzelian theory.

The transition from the view of the constitution of sal ammoniac just described, to the corresponding theory of the salts with oxygen acids, is very simple, and will not require much exposition. Giving to the oil of vitriol the formula $\mathrm{SO}_4 + \mathrm{H}$, it will at once result that hydrogen combinations of that form should as easily unite with the amidide of hydrogen as with any of the corresponding oxides; and hence the ordinary sulphate of ammonia becomes $\mathrm{H.SO}_4 + \mathrm{HA}d$, the nitrate of ammonia $\mathrm{HNO}_6 + \mathrm{HA}d$. In its common form the sulphate of ammonia assumes two equivalents of water, and becomes $\mathrm{H.SO_4 + HA}d\mathrm{.HO}$, with which very many analogues will be found. Thus in the magnesian class we find the sulphate of copper uniting with ammonia in a similar manner to form the body $\mathrm{C}u\mathrm{SO_4. + HA}d$. In nickel there is $\mathrm{N}i\mathrm{.SO_4 + HA}d$; and in the zinc combinations there is not merely $\mathrm{Z}n\mathrm{SO_4 + HA}d$, but $\mathrm{Z}n\mathrm{SO_4 + HA}d\mathrm{.HO}$, resembling in constitution the ordinary sulphate of ammonia. It is very much to be regretted that the circumstance of water decomposing these bodies prevents the question of their isomorphism with the ordinary ammonia salts from being fully determined, but it is not improbable that future research may enable some instances to be examined.*

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* In the Jahresbericht for 1837, (17th year,) page 139, Berzelius, in commenting on the interesting results of Heinrich Rose on the combinations of dry sulphuric acid and the chlorides of the alkaline metals, &c., speaks of the combination of sulphuric acid and sal ammoniac in the following terms, which, that work being but little circulated in Ireland, I shall here translate, as the opinions of that eminent chemical philosopher must affect considerably the judgment of chemists concerning the views which I have proposed.

" These facts are of great theoretical interest. They appear, if not expressly to answer, at least to give indications for the solution of a great variety of questions. That, for example, whether sal ammoniac consists of muriatic acid and ammonia, or of the metallic body, ammonium, and chlorine. The great analogy between chloride of potassium and sal ammoniac seems to me to speak plainly enough in this question, but distinguished chemists appear not to approve of this evidence, and prefer the former view as the more probable. If we consider the action of dry sulphuric acid on sal ammoniac as a new form of the question put in order to compel an answer, the answer given must negative the view of hydrochlorate of ammonia. Dry sulphuric acid, combined with ammonia, cannot be expelled by muriatic acid, and consequently has a greater affinity for it than the latter. It is hence clear, that if muriatic acid were present in sal ammoniac it should be expelled by the dry sulphuric acid. On the contrary, however, the acid unites with the sal ammoniac, and forms a body, which in all its relations corresponds to the compounds of the acid with the chlorides of potassium and sodium, and it is only by a higher temperature being applied that decomposition sets in, and there are formed dry sulphate of ammonia and free hydrochloric acid. My view may be rather keen-edged, but it appears to me that these experiments of Rose's declare with positive openness the sal ammoniac to be chloride of ammonium, and not hydro-chlorate of ammonia."—Page 141.

If we look upon the relation between ammonia and chloride of hydrogen as being in accordance with the old view, that of acid to base, then the criticism of Berzelius must be considered as possessing very considerable accuracy and force. But it has been my great object in the present section to show, that our views in this respect require a profound alteration. When we apply to the explanation of Rose's results the lights which we receive, in addition, from the change in our point of view, and that we consider the oxyamidide and chloro-amidide of hydrogen as related to each other, like

Prop. VI.—*That the ordinary ammonia salts ally themselves to the salts of the copper and zinc class, which contain two equivalents of oxide.*

The subject of this proposition is one of the most remarkable which I have been induced to adopt in the course of these researches, and the nature of the evidence in its favour will require a cautious and detailed examination of the individual instances of replacement by which it is supported.

I have pointed out already, briefly, that all those ammonia-copper, zinc, and nickel combinations which are formed by solution in water, must be looked upon as combinations of ordinary ammoniacal salts with metallic oxide and amidide of hydrogen, as well as occasionally still more water, at least in their crystallized condition. As the establishment of this principle becomes of great importance, I shall again sum up the proofs of it, and notice one or two examples, which were not at that time alluded to. The progress of the reaction, in which at first a pure ammoniacal salt and a basic metallic compound is always formed, indicates the nature of the resulting body very remarkably; and when we consider that the bodies generated by dry ammoniacal gas were in all cases quite different, the evidence becomes almost complete; likewise, where we find that in the quicksilver compounds the formation of the ammonia-quicksilver body occurs from the commencement, and we cannot trace any stage at which the deposition of a sub-

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chloride and oxide of potassium, it appears quite natural that sal ammoniac should combine with acids, as chloride of potassium does in some instances, and that there should be $SO_3 + (HCl + HAd)$ as there is $SO_3 + (HO + HAd)$ equivalent to $2CrO_3 + KO$ and $2CrO_3 + KCl$. On this view there is no reason for the expulsion of chloride of hydrogen as being the weaker acid, but by heat the expulsion of HCl can easily be understood. We cannot, by heating $SO_3 + HO.HAd$, expel HO, without other effects complicating the result; but the reaction in the case of $SO_3 + HCl.HAd$ takes place with greater ease and completeness. The compound $SO_3 + HCl$, formed by Aimé, though not analyzed, evidently resembles $SO_3 + HO$; and by the addition of ammonia a compound of an equivalent character should be produced. Another similar case is the brown powder, $SO_3 + (CuO + HCl)$, which, when heated, gives $SO_3 + CuO$ and $H.Cl$, as there are $SO_3 + CuO.HO$ and $SO_3 + CuO.HAd$, which give precisely similar results. Berzelius appears to have understood from my description, that when dry ClH is passed over dry $CuO.SO_3$, the brown mass becomes moist from free sulphuric acid; that, however, is not the fact, water is set free only when the sulphate of copper is not dry; the brown mass does not fume nor grow damp; it does not give any indication of free acid. The body $SO_3 + CuO.ClH$ is perfectly definite and well characterized.

stance free from ammonia has occurred, some fundamental distinction must necessarily be drawn between the resulting ammonia bodies of the mercurial series and those containing copper, zinc, or nickel.

A remarkable example of this kind is furnished by nitrate of silver. When dry ammonia is passed over nitrate of silver it is absorbed in quantity, but by the application of a moderate heat it can be all again expelled. If an excess of water of ammonia be added to nitrate of silver there is obtained the crystalline compound analyzed by Mitscherlich and myself, and which, when heated, gives common nitrate of ammonia, metallic silver, and the elements of amidogene. Thus there are two bodies,

1. $\mathrm{A}g\mathrm{O}.\mathrm{NO}_5 + 3\mathrm{NH}_3$.
2. $\mathrm{HO}.\mathrm{NO}_5.\mathrm{NH}_3 + \mathrm{A}g.\mathrm{A}d$.

And in the latter case the formation of the common ammoniacal salt and of the metallic amidide becomes quite manifest.

Recurring to the constitution of the ammonia sulphate of copper, there is

1. $\mathrm{HO}.\mathrm{SO}_3.\mathrm{HA}d + \mathrm{C}u\mathrm{O}.\mathrm{HA}d$.

In the zinc series there is

2. $\mathrm{HO}.\mathrm{SO}_3.\mathrm{HA}d + \mathrm{Z}n\mathrm{O}.\mathrm{HA}d + 2\mathrm{HO}$.

In the nickel series,

3. $\mathrm{HO}.\mathrm{SO}_3.\mathrm{HA}d + \mathrm{N}i\mathrm{O}.\mathrm{HA}d + \mathrm{HO}$.

Here a property is found fully displayed, which in the ordinary ammonia salts is either latent, or else but feebly manifested, except when in combination; that is, the power of combining with water of crystallization, or with a group of equivalents of the same type, and capable of representing such. If we set out from the common sulphate of potash, and one form of sulphate of ammonia, quite anhydrous, the second gives to us in $\mathrm{HO}.\mathrm{SO}_3.\mathrm{HA}d + \mathrm{HO}$ the commencement of the series, the completion of which, for the ordinary salts of ammonia, must be sought in the common alums, where there is

$$(\mathrm{HO}.\mathrm{SO}_3.\mathrm{HA}d + 6\mathrm{HO}) + (\mathrm{A}l_2\mathrm{O}_3.3\mathrm{SO}_3 + 18\mathrm{HO}),$$

and in which $\mathrm{KO}.\mathrm{SO}_3$ is similarly circumstanced.

The complex group, partly metallic oxide and partly ammonia, which occupies one portion of the formula, leads naturally to the study of still more remarkable cases of the operation of these principles.

The bodies

1. $HO.SO_3.HAd + HO.$
2. $HO.SO_3.HAd + ZnO.$
3. $CuO.SO_3.HAd.$
4. $ZnO.SO_3.HAd.$

and in the quicksilver compounds,

5. $HgO.NO_5.HAd + 2HgO.$
6. $HgO.NO_5.HgAd + 2HgO.$
7. $HgO.SO_3.HgAd + 2HgO.$

present to our view a series passing from common sulphate of ammonia to ammonia turbith, in which the successive stages of replacement of hydrogen by metal are so connected, and follow so naturally, that it appears to me very difficult to refuse consent to the proposition that the latter members are constituted on the type of the former, and consequently that we may have forms of ammonia salts, in which the oxygen and amidogene are combined, not with hydrogen, but with metal, and in which, therefore, the peculiarly basic character should preponderate.

If we now for a moment contemplate the formula of a double ammonia sulphate of that class, whose history has been cleared up by Graham, it will be found that some considerations of a most interesting nature will result from their relations to the group last noticed. The double sulphate of copper and ammonia is

$$HO.SO_3.HAd + CuO.SO_3 + 4HO.$$

Graham had himself suggested the following form for the ammonia sulphate of copper described by Rose,

$$CuO.SO_3.HAd + CuOSO_3 + 4HAd,$$

but only as a speculation, the state of our knowledge of the ammonia compounds then not allowing the proper demonstration of its truth. The majority of sulphates absorb, however, a whole number of equivalents of ammonia, thus there is

1. $ZnO . SO_3 . HAd + 2 HAd.$
2. $CdO . SO_3 . HAd + 2 HAd.$
3. $NiO . SO_3 . HAd + 2 HAd.$
4. $CoO . SO_3 . HAd + 2 HAd.$

evidently corresponding to

5. $ZnO . SO_3 . HO + 2 HO$, &c.

The close relation which has been thus shown to exist between the most intimately united portion of the amidide of hydrogen and of the constitutional water of the magnesian class of sulphates, may be rendered still more remarkably evident from the following examples.

Anthon has discovered a peculiarly hydrated condition of the sulphate of zinc, which has the formula $ZnO . SO_3 + 3\frac{1}{2} HO$. It crystallizes in rhomboids, of which the exact form has not been determined; this salt appears to be produced under circumstances not yet completely known, but it would be most interesting to ascertain exactly its crystalline admeasurement. I consider that the halving of the equivalent of water in this salt results from precisely the same law as the absorption of half an equivalent of ammonia by dry sulphate of copper, and that its formula should be

1. $ZnO . SO_3 . HO + ZnO . SO_3 + 6 HO$,

the ammonia zinc sulphate being

2. $HO . SO_3 . HAd + ZnO SO_3 + 6 HO.$

In this salt, as I could not produce it at will, it was impossible to determine whether the half atom of water was more powerfully retained, so as to give the dry double salt

3. $ZnO . SO_3 . HO + ZnO . SO_3$,

as there is

4. $CuO . SO_3 . HAd + CuO SO_3$;

but every thing would lead us to suppose it to be in a state of combination differing from the rest.

In a family of the salts differing but very little from the ordinary alums, there will be found some very remarkable examples of the similarity of action of two equivalents of a magnesian protoxide, with oxide of kalium, or ammonia and water. This family was discovered by Klauer, who formed double sulphates of alumina with the protoxides of iron and nickel, with magnesia and oxide of zinc; and lately one of the most remarkable examples of this class, a double sulphate of alumina and protoxide of manganese was found forming a thick bed on the coast of Africa, and brought to this country, where it has been analyzed by Apjohn and by myself.

The general formula of this class, as has been accurately determined with the manganese and zinc members, is as follows: RO = protoxide,

$$1.\ (\mathrm{RO}\,.\,\mathrm{SO_3}\,.\,\mathrm{HO}) + (\mathrm{A}l_2\mathrm{O_3} + 3\,\mathrm{SO_3}) + 24\,\mathrm{HO},$$

resembling accurately

$$2.\ (\mathrm{HO}\,.\,\mathrm{SO_3}\,.\,\mathrm{HA}d) + (\mathrm{A}l_2\mathrm{O_3} + 3\,\mathrm{SO_3}) + 24\,\mathrm{HO},$$

which it further assimilates itself to in taste and solubility.

The relation of the water of these alums to heat is very remarkable, and indicates very accurately the nature of their constitution. Thus by a temperature of 212°, eighteen equivalents of water are lost; by a heat of 300° there are given out six more; but the expulsion of the remaining equivalent requires a temperature equal to the melting point of lead, indicating the intenseness of the power with which it is retained; in fact the zinc alum may be looked on as composed of ordinary sulphate of zinc and ordinary sulphate of alumina,

$$\begin{array}{c}
\mathrm{Z}n\mathrm{O}\,.\,\mathrm{SO_3}\,.\,\mathrm{HO} + 6\,\mathrm{HO} \\
\mathrm{A}l_2\mathrm{O_3}\,.\,3\,\mathrm{SO_3} + 18\,\mathrm{HO} \\
\hline
\mathrm{Z}n\mathrm{O}\,.\,\mathrm{SO_3}\,.\,\mathrm{HO} + \mathrm{A}l_2\mathrm{O_3}\,.\,3\,\mathrm{SO_3} + 24\,\mathrm{HO}.
\end{array}$$

The form $\mathrm{M}n\mathrm{O}\,.\,\mathrm{SO_3}\,.\,\mathrm{HO} + 6\,\mathrm{HO}$ is not the ordinary condition of proto-sulphate of manganese, but it also can be obtained with that quantity of water.

The preceding considerations showing, with considerable probability, that two equivalents of an oxide of the magnesian class may replace in combination, and even affect isomorphism with an equivalent of the alkaline group, it may be proper to inquire how far evidence capable of illustrating the theory under examination can be collected from amongst the numerous species of minerals which are supposed to present cases of replacement of an alkali by an earth. In such cases the substitution may take place in two ways, which renders the demonstration of its occurrence much more difficult than it might at first be supposed; in the first class, the substituting equivalents being oxides of the same, in the second they being oxides of different bases. Thus in the former, two atoms of lime, magnesia, or of water; in the latter, one of lime and one of water, or one of magnesia and one of water, likewise lime and magnesia without water, lime and protoxide of iron, &c. The complication thus arising must render new researches for the determination of the point not only necessary, but very difficult; and hence, although I would look very sanguinely to a re-examination of the harmatome and zeolitic groups for a great accession to our accurate knowledge of this department of science, I have not been able to deduce from analyses at present recorded any definite results, except in one instance, which, however, in itself may be almost looked upon as conclusive.

This example consists in the group of minerals consisting of natrolite, mesolite, and scolezite, which constitute one of the best instances of isomorphism that has been as yet found, and are related to each other in constitution in a very simple manner: the natrolite being a hydrated silicate of soda and alumina, the scolezite being a hydrated silicate of lime and alumina, and the mesolite, probably a product of the crystallizing of the two together, being intermediate in constitution. Now the formulæ accurately given by analyses for the pure species are, thus,

$$\mathrm{N}ao\,.\,\mathrm{S}io_3 + \mathrm{A}l_2o_3\,.\,\mathrm{S}io_3 + 2\,\mathrm{HO}$$

and

$$\mathrm{C}ao\,.\,\mathrm{S}io_3 + \mathrm{A}l_2o_3\,.\,\mathrm{S}io_3 + 3\,\mathrm{HO},\text{ or better,}$$
$$\mathrm{C}ao\,.\,\mathrm{HO}\,.\,\mathrm{S}io_3 + \mathrm{A}l_2o_3\,.\,\mathrm{S}io_3 + 2\,\mathrm{HO}.$$

Here the equivalency of $\mathrm{C}ao\,.\,\mathrm{HO}$ to $\mathrm{N}ao$ is most remarkable, and certainly must be allowed to go a great way towards confirming the views regarding the nature of the compounds of ammonia, from which the analogy of $\mathrm{NH_2.H}$ to $\mathrm{H.O}$, and hence to $\mathrm{C}ao$ or $\mathrm{M}go$, and of $\mathrm{NH_4O}$ to $\mathrm{C}ao\,.\,\mathrm{HO}$, &c. was first arrived at.*

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* Since the above views were completely formed, and the memoir read, I was singularly struck by finding in the Elemente der Crystallographie of Gustav Rose, the same view suggested of the replacement of soda, not by lime, but by its hydrate. Intending to commence an examination of the zeolitic group under the point of view noticed above, I began by the study of their crystallographic relations, to which I had not before applied myself, and selected his work as the system best adapted to my purpose. In speaking of the composition of wernerite, (page 158,) the following passage occurs, which, as the work is not very common in Ireland, I shall translate. "The above

During the examination of the various classes of compounds of ammonia, which the objects of these researches rendered necessary, a variety of results were obtained, which are calculated to throw light on the relation in which the ammoniacal salts stand to the ordinary basic salts of the same acid, and likewise to illustrate the connexion between the corresponding so called neutral and basic salts. In the cases of the nitrates of mercury, my observations have the effect of extending to that metal the law discovered by Graham for the nitrates of the metals of the magnesian class, but as that distinguished chemist has not deduced any general idea of the constitution of the basic sulphates from his observations, I shall briefly suggest such ideas as have occurred to me from my own investigations.

The general principle that the transition from the neutral to the basic condition in salts takes place by the replacement of water by metallic oxide, has, as I conceive, received the fullest confirmation; but I do not consider that the corresponding substitution of water for metallic oxide, which exists so markedly in the sub-nitrates of copper and bismuth can be looked upon as forming a general law. Thus there certainly does not appear the same perfect symmetry between

$$\mathrm{HO.NO_5} + 3\mathrm{H}g\mathrm{O} \text{ and } \mathrm{H}g\mathrm{O.NO_5} + \mathrm{H}g\mathrm{O} + 2\mathrm{HO}$$

as between

$$\mathrm{C}u\mathrm{O.NO_5} + 3\mathrm{HO} \text{ and } \mathrm{HO.NO_5} + 3\mathrm{C}u\mathrm{O};$$

and although I do not possess absolute proof of the existence of a sub-nitrate

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formula is that which Hartwell has established. According to his analyses, lime and soda replace one another in indeterminate proportions, and are consequently placed in the formula under one another, as isomorphous bodies, although there is not as yet known any positive example of the isomorphism of lime and soda. The sulphate of soda or thenardite does not appear to be isomorphous with anhydrite, and the analyses of mesotype by Gehlen and Fuchs, show perfectly that lime and soda may replace each other, but that in this case, the quantity of water in the compound also changes, so that one atom of soda can be isomorphous only with an atom of lime + an atom of water, which must consequently be assumed in all other zeolites where lime and soda appear to replace each other, as, for example, in the chabazies." It is singularly interesting to find, that starting from an origin apparently so remote as the composition of white precipitate, I have been gradually conducted to the development of the same principle as had already, though unknown to me, been announced, even though but as a suggestion, by an authority so deservedly high in chemistry and mineralogy as Gustav Rose.

having the four equivalents of oxide all alike, yet I cannot consider such an arrangement as being excluded.

Indeed an idea which was suggested to me by the mercurial nitrates is, that the constitution of the nitrates may be better shown by writing the formula of their class as follows:

$$RO . NO_5 . RO + 2RO.$$

R being either water or metallic oxide. There is then

$$HgO . NO_5 . HgO + 2HO,$$
$$HgO . NO_5 . HO + 2HgO,$$

and the red basic nitrate,

$$HgO . NO_5 . HgO + 2HgO + 2HgO.$$

and still further,

$$HgO . NO_5 . HAd + 2HgO,$$
$$HgO . NO_5 . HgAd + 2HgO.$$

As in the copper and bismuth nitrates, no water whatsoever can be separated without a corresponding quantity of acid being set free, it is difficult to ascertain whether one atom of the water is more firmly attached to the acid than the other two; but in the case of nitrate of magnesia, Graham has found that two of the equivalents of water may be separated much more easily than the third, and hence its formula should be, as in the quicksilver series,

$$MgO . NO_5 . HO + 2HO.$$
$$MgO . NO_5 \; HO + 2MgO.$$

Thus connecting still further mercury with the metals of the magnesian class. This form of expression for the nitrates connects them much more closely with the sulphates than the older view, and the equivalent to the right of the acid evidently replaces the saline water of the magnesian sulphates. Thus a sulphate of that group is generally, though not always,

$$RO . SO_3 . HO + 2nHO,$$

n being a whole number.

In the sulphates the most common form of basic constitution approaches still more closely to the type of basic nitrates than in the neutral state; thus,

$$1.\ \mathrm{cuo\ .\ so_3\ .\ cuo + 2cuo.}$$
$$2.\ \mathrm{zno\ so_3\ .\ zno + 2zno.}$$

which are those most easily formed, and most permanent.

A great number of circumstances conspire to render the derivation of the basic sulphates of the magnesian class, from the neutral condition, exceedingly complicated. Thus the neutral salts crystallize with quantities of water variable within very extensive limits, and the proportion of metallic oxide by which it may be replaced, is subject to fluctuations equally wide: moreover, the replacement of the water by metallic oxide may be but partial, and hence the different hydrated conditions in which the basic salts exist. From these causes may be deduced the possible existence of a very extensive series of basic sulphates varying considerably in type, and subject only to the one restriction, that in all their different conditions the sum of the equivalents of water and metallic oxide shall always be equal to the sum of the same constituents in some one of the forms in which the neutral salt may crystallize. So that the general expression of the class becomes

$$\mathrm{ro\ .\ so_3\ .} \left.\begin{matrix}\mathrm{r}\\ \mathrm{h}\end{matrix}\right\}\mathrm{o} + 2n \left.\begin{matrix}\mathrm{r}\\ \mathrm{h}\end{matrix}\right\}\mathrm{o.}$$

$\left.\begin{matrix}\mathrm{r}\\ \mathrm{h}\end{matrix}\right\}$ indicating the sum of the mutually replacing elements. In the synopsis of the analytical results of the basic sulphates contained in the sections on the copper and zinc compounds, the instances given can be so immediately compared with the above expression, that it is not necessary to reinsert them here.

Although the general form of the crystallized chlorides of the magnesian group of metals, as was well shown by Graham, consists in the adhesion of pairs of equivalents of water, yet in the construction of the basic chlorides or chloroxides the form pointed out for the nitrates and some basic sulphates is adopted; thus, the ordinary chloride of copper, $\mathrm{cu}cl + 2\mathrm{ho}$, cannot be obtained in combination with more water, but the tendency to assume the fourth molecule is shown in its basic forms, thus it may become

$$\mathrm{cu}cl + 2\,\mathrm{cuo},$$

and thence

$$\mathrm{cu}cl + 2\,\mathrm{cuo} + \mathrm{cuo}$$
$$\mathrm{cu}cl + 2\,\mathrm{cuo} + \mathrm{ho}$$
$$\mathrm{cu}cl + 2\,\mathrm{cuo} + \mathrm{ha}d$$

as has been already noticed in another point of view.

In quicksilver there is the oxychloride

$$Hgcl + 2\,Hgo + Hgo,$$

and then

$$Hgcl + 2\,Hgo + HgAd$$

evidently corresponding; but in most instances the basic chlorides follow, like the sulphates, the form of the hydrated neutral conditions, and hence there is

$$zncl + 6\,zno$$
$$cucl + 4\,cuo$$
$$cucl + 2\,cuo$$

as there are two, four, or six atoms of water in the crystallized conditions of various chlorides.

Prop. VII.—*That if chlorine could be separated from sal ammoniac, the residual* NH_4 *should be regarded as* $NH_2 + 2\,H$, *sub-amidide of hydrogen, as when by removing the chlorine from white precipitate, the sub-amidide of mercury,* $NH_2 + 2\,Hg$, *formed by the action of water of ammonia on calomel, should remain.*

The discussion of this proposition leads to some considerations as to the nature of the so called compound radicals, which of late years have played so distinguished a part in the progress of chemical philosophy. The views which I shall put forward I offer with considerable hesitation, as not resting directly upon experimental evidence, but resulting from the peculiar manner in which my researches have induced me to contemplate the nature of those hypothetic bodies.

The fundamental idea that a compound body might so manifest its affinities as to simulate the properties of an undecompounded substance, received its first conception, as well as proof, from the beautiful discovery of cyanogen by Gay Lussac, which continues even up to the present day the most glaring instance of the truth, as well as the most excellent example of the nature of the theory of compound radicals.

The extension of the principle involved in the very existence of cyanogen, to explain the constitution of classes of bodies of organic origin presenting strong analogies to the cyanides, although the compound radicals of their series could not be successfully isolated, gave to the theory of organic chemistry great clearness and consistency, and was indeed philosophically just, since from the facility of decomposition of cyanogen in a variety of ways, we must infer that many bodies of similar nature may be so much more easily decomposed, that in our ordinary modes of operating on them their preservation becomes impossible, precisely as the existence of cyanogen had escaped the acuteness of Proust, of Berthollet, and others, who had experimented on prussic acid at former times. I therefore do not hesitate to place the theory of compound radicals amongst the greatest benefits which chemistry has lately received, and hope with confident expectation for the addition of very many new examples to the list, hitherto restricted to cyanogen and mellon.

But what is the constitution of a compound radical? does it consist of a group, beyond which we cannot go without reducing it to its merely undecomposable constituents? or has it, again, a symmetricity of constitution like the whole mass from which it had been eliminated. I shall not touch upon this question as affecting cyanogen, benzoyl, or similar bodies, limiting myself altogether to the examination of how far our ideas of the nature of ammonium may be affected by that point of view.

In sal ammoniac, the chlorine is certainly united with a body which replaces potassium, and if we could discover circumstances under which the chlorine might be transferred to another substance, leaving all the hydrogen and azote undisturbed, then the ammonium would be isolated; but let us examine what this ammonium should be. The sal ammoniac is chlor-amidide of hydrogen. If the chlorine were removed, the amidogene should remain combined evidently with twice as much hydrogen as constitutes ammonia, and this body, sub-amidide of hydrogen, might well be able to represent in combination, and to combine with, metals. This partial participation in metallic properties is found in other sub-combinations, as in the sub-oxides of copper and of mercury, and hence the generation of the ammoniacal amalgam, its low specific gravity, the sub-amidide of hydrogen being probably gaseous: an extension of this view might illustrate the condition of the isomorphism of two equivalents of one oxide with one of another, (as pointed out in the alums and certain minerals in the last proposition,) the former, perhaps, assuming the form O (ROR): the sub-oxide represented in the brackets relating itself as a compound radical to the oxygen outside. Hence, likewise, a consideration of the problem, whether a second oxide be a combination of metal with oxygen, or of oxygen with the first oxide, which I must consider as decided by the circumstance of the atomic weight containing one or two equivalents of oxygen. Thus I look upon the study of the salts of mercury as decisive upon the red oxide of that metal being protoxide, but the examination of the compounds of manganese assigns to the black oxide the form $(Mn O)+O$.

A remarkable fact in the history of the alkaline salts suggests an extension of the views here discussed, which is thrown out as a speculation, and to which I do not wish to attach otherwise importance. The sulphate of ammonia may be written on the ammonium theory, $SO_3+O.(NH_4)$, or $SO_3+O(HAd H)$; and the ammonium being a basic amidide, it results that the ammoniacal salts are all basic salts; hence the condition which the salts of the magnesian class may be made artificially to assume is that naturally belonging to those of the ammoniacal series. Now as the ammonia and potash salts assimilate so completely, the speculation may be hazarded, that research will discover in potassium a structure analogous to that which I have argued to exist in the so called ammonium, and the result may show that the reason of the alkalies not producing basic salts, arises from the circumstance of their salts being already basic in their common form.

SUPPLEMENTARY NOTE

ON A COMPOUND HITHERTO CONSIDERED AS WHITE PRECIPITATE.

SOME time since I learned that Professor Woehler had found that the white precipitate in the possession of some Hanoverian apothecaries differed in many important particulars from that which formed the subject of my researches, as well as of the experiments of verification made by Ullgren. The body in question had been prepared by precipitating a solution of sal alembroth by potash in the cold. The precipitate which is produced, resembles externally the true white precipitate so completely as to have been always taken for it, and hence in many pharmacopœias this process is given for preparing white precipitate for medicinal purposes. It is, however, quite different in its nature, and as its analysis is of importance as well in a practical as in a theoretical point of view, the following brief description of its nature is subjoined:

When heated it fuses into a clear liquid, giving off at the same time azote and ammonia, but no water, if the precipitate had been completely dried. The fused substance sublimes ultimately in a mass partly transparent like gum, and partly white and opaque. When the sublimed mass is treated with water, it in part dissolves, calomel remaining undissolved, the solution is neutral, and on examination is found to contain sal ammoniac and sublimate. If this new white precipitate be boiled in water there results the same yellow powder, which is produced by boiling the genuine white precipitate; but the sal ammoniac is formed in the liquor in much larger quantity.

The methods of analysis pursued were precisely the same as those described in the memoir on white precipitate, and consequently it is unnecessary to repeat the details of them here. The results of three analyses were:

		I.	II.	III.
Mercury	=	65.42	66.27	65.74
Chlorine	=	22.05	22.70	22.95
Ammonia	=	10.65	11.01	10.94
		98.12	99.98	99.63

These numbers lead directly to the formula $\mathrm{Hg}cl + \mathrm{NH}_3$, which should give

Hg	=	101.40	65.86
cl	=	35.42	23.01
NH_3	=	17.14	11.13
		153.96	100.00

This body may therefore be looked on as consisting of an atom of sublimate and one of ammonia. Now the result of passing ammonia over sublimate is to generate a white substance, $2cl\mathrm{Hg} + \mathrm{NH}_3$, which is evidently a kind of double chloride, $\mathrm{Hg}cl + \mathrm{HgAd}\mathrm{H}.cl$, similar to many bodies already noticed in these researches, as

$$zncl + zn\mathrm{Ad}.\mathrm{H}cl$$
$$cu\mathrm{SO}_4 + cu\mathrm{Ad}.\mathrm{HSO}_4$$

This body is likewise of interest, as standing midway between sal ammoniac and the real white precipitate, and serving to link bodies apparently so dissimilar still more closely to the principles of the theory of the ammonia compounds developed in the present memoir; the chlor-amidide of hydrogen, $HCl + HAd$, and the chlor-amidide of mercury, $HgCl + HgAd$, being connected by the intermediate chlor-amidide of mercury and hydrogen, $HgCl + HAd$.

I had remarked long since, that by the addition of sal ammoniac to the water in which the real white precipitate is boiled, its decomposition, or at least the formation of the yellow powder is prevented. The white precipitate remains white, but its nature is totally altered; it is converted altogether into the new compound, and it will be seen that its composition would be represented, supposing it to be formed by the union of the two substances which had been put in contact, for $2\,(HgCl.NH_3) = (HgCl.HgAd + HCl.HAd)$.

Such a mode of representing its nature would likewise explain its various properties, but I prefer the view first described, and look upon this body as simply expressed by $HgCl + HAd$. I would propose for it the empirical name of Woehler's white precipitate, and if one founded on composition be deemed necessary, that of the hydrargyro-chlor-amidide of hydrogen.

A reaction which I have lately observed, and which as a remarkable property of white precipitate, is worthy of being noticed, is, that when the chlor-amidide of mercury is boiled with an excess of chloride of copper, it is totally converted into sal alembroth, and there results brunswick green. The reaction appears to be as follows:

$$8\,CuCl + 3(HgCl + HgAd) + 6\,HO = 2(CuCl + 3\,CuO) + 3(2\,HgCl + NH_4Cl).$$

In the sal alembroth thus produced the proportions of its ingredients are different from those of the more common form: the sublimate containing twice as much chlorine as the sal ammoniac. It is, however, quite definite, and can be easily procured by dissolving together sublimate and sal ammoniac in the proper quantities. It crystallizes in two forms, one rhomboidal, the other in long silky needles; in the former condition the salt is dry, in the latter it retains an equivalent of water. Frequent analyses gave for their composition the formulæ

Rhomboidal state $= 2\,HgCl + NH_4Cl$.
Fibrous state $= 2\,HgCl + NH_4Cl + HO$.

The ordinary form being, as is well known, $HgCl + NH_4Cl + HO$.